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XXIV. *Properties of Substances in the Condensed State at the Absolute Zero of Temperature.* By R. D. KLEEMAN, D.Sc., Consulting and Research Physicist and Physical Chemist, Associate Professor of Physics, Union College, Schenectady, N.Y.*

IN a previous paper (Phil. Mag. iii. p. 883, 1927) the writer showed that the internal energy and entropy of a substance or mixture may each be divided into two parts, one of which is externally controllable while the other is not. It was also shown that the controllable entropy and internal energy are each zero when the substance or mixture is in the condensed state at the absolute zero of temperature. This zero was called for convenience the absolute zero of control. It was also shown that the relations

$$\left(\frac{\partial U}{\partial v}\right)_T = 0, \quad (1)$$

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v = 0, \quad (2)$$

$$. \left(\frac{\partial S}{\partial v}\right)_T = 0, \quad (3)$$

$$\left(\frac{\partial S}{\partial T}\right)_v = 0 \quad (4)$$

hold under these conditions, where U denotes the controllable internal energy, S the controllable entropy, c_v the specific

* Communicated by the Author.

heat at the constant volume v , and T the absolute temperature. A number of additional relations will be deduced in this paper from the results already established and well-known thermodynamical formulæ by means of the differential calculus and the postulate that $\frac{\partial^{n+m}p}{\partial v^n \cdot \partial T^m}$ (where p denotes the pressure) cannot be infinite, which follows from our notions of matter. The importance and use of these relations consist in that they must be satisfied by the general relations holding between the various quantities on writing $T=0$ and $v=v_0$, where v_0 denotes the volume of the substance or mixture in the condensed state at the absolute zero of temperature.

1. From thermodynamics we have

$$\left(\frac{\partial U}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p, \quad . \quad . \quad . \quad (5)$$

where U may be taken to refer to the controllable internal energy, since the uncontrollable part, which is not a function of v and T , would disappear through differentiation. On differentiating this equation with respect to T , and n times with respect to v , it becomes

$$\frac{\partial^{n+1}U}{\partial v^n \cdot \partial T} = \left(\frac{\partial^n c_v}{\partial v^n}\right)_T = T \frac{\partial^{n+2}p}{\partial v^n \cdot \partial T^2} \quad . \quad . \quad . \quad (6)$$

The factor of T in this equation is not infinite according to the postulate given, and hence for a substance or mixture in the condensed state at the absolute zero of temperature, or at the absolute zero of control of the substance or mixture, we have

$$\frac{\partial^{n+1}U}{\partial v^n \cdot \partial T} = \left(\frac{\partial^n c_v}{\partial v^n}\right)_T = 0, \quad . \quad . \quad . \quad (7)$$

since $T=0$. The specific heat will possess this property if it can be expressed by the equation

$$c_v = \phi_1(v, T) \cdot \phi_2(T), \quad . \quad . \quad . \quad (8)$$

where $\phi_2(T)=0$ when $T=0$. It possesses then also the property expressed by equation (2). It should be noted, however, that c_v may have the property expressed by equation (7) without having the form given by equation (8).

Every specific heat equation obtained from quantum and other considerations should obey equation (7). A test of the correctness of the assumptions underlying the equation is thereby afforded.

2. Equation (4) may be written

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_v = \frac{0}{0}$$

at the absolute zero of control according to equation (2), and since $T=0$. By means of the differential calculus the limiting form on the right-hand side of the equation may be written

$$\left(\frac{\partial S}{\partial T}\right)_v = \left(\frac{\partial^2 U}{\partial T^2}\right)_v,$$

and therefore according to equation (4)

$$\left(\frac{\partial^2 U}{\partial T^2}\right)_v = \left(\frac{\partial c_v}{\partial T}\right)_v = 0. \quad . \quad . \quad . \quad . \quad (9)$$

We have seen in the paper quoted that equation (2), which is Nernst's specific heat theorem at constant volume, follows directly from thermodynamics. Equation (9) expresses another property of the specific heat, namely, that its first differential with respect to the temperature is zero, which also depends directly on thermodynamics. Experimental evidence of its truth already exists. According to Debye's formula for the specific heat of a monatomic solid *, which is found to agree well with the facts, the specific heat near the absolute zero of temperature is given by

$$c_v = aT^3, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where a is a constant. This equation has been specially investigated by Kammerlingh Onnes and found to be in close agreement with experiment †. It evidently agrees with equation (9). It is highly desirable that experiments be also carried out with mixtures near the absolute zero of temperature, to determine if their specific heats also satisfy equations (2) and (9), as they should if the deductions on which the equations rest are sound.

3. Equation (4) may be written

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_v = 0,$$

which, on being differentiated with respect to T , becomes

$$\left(\frac{\partial^2 S}{\partial T^2}\right)_v = \frac{1}{T} \left(\frac{\partial^2 U}{\partial T^2}\right)_v - \frac{1}{T^2} \left(\frac{\partial U}{\partial T}\right)_v = \frac{0}{0} - \frac{0}{0},$$

the right-hand side assuming a limiting form on account of

* *Ann. Physik* (4) xxxix. p. 789 (1912).

† *Comm. Phys. Lab., Leiden*, No. 147 (1915).

equations (2) and (9). and since $T=0$. On obtaining the value of the limiting form by means of the differential calculus the equation becomes

$$\left(\frac{\partial^2 S}{\partial T^2}\right)_v = \frac{1}{2} \left(\frac{\partial^3 U}{\partial T^3}\right)_v \dots \dots \dots (11)$$

It expresses a relation between S and U at the absolute zero of control.

4. On differentiating equation (5) with respect to v it becomes

$$\left(\frac{\partial^2 U}{\partial v^2}\right)_T = T \frac{\partial^2 p}{\partial v \cdot \partial T} - \left(\frac{\partial p}{\partial v}\right)_T.$$

Since $T=0$ and its factor is not infinite according to the postulate given, the equation should be written

$$\left(\frac{\partial^2 U}{\partial v^2}\right)_T = - \left(\frac{\partial p}{\partial v}\right)_T \dots \dots \dots (12)$$

The right-hand side may be evaluated by means of the equation of state, remembering that $T=0$ and $v=v_0$, where v_0 denotes the volume of the substance or mixture in the condensed state at the zero of control. Similarly it can be shown that

$$\left(\frac{\partial^n U}{\partial v^n}\right)_T = - \left(\frac{\partial^{n-1} p}{\partial v^{n-1}}\right)_v \dots \dots \dots (13)$$

5. In general we have

$$\partial S = \frac{1}{T} (\partial U + p \cdot \partial v),$$

which may be written

$$\left(\frac{\partial S}{\partial v}\right)_T = \frac{1}{T} \left(\frac{\partial U}{\partial v} + p\right) = \left(\frac{\partial p}{\partial T}\right)_v \dots \dots \dots (14)$$

by means of equation (5). On differentiating this equation $n-1$ times with respect to v we have

$$\frac{\partial^n S}{\partial v^n} = \frac{\partial^n p}{\partial v^{n-1} \cdot \partial T} \dots \dots \dots (15)$$

The right-hand side of this equation may be evaluated by means of the equation of state. It is of interest to compare this equation with equation (13).

6. For an adiabatic change we have directly that

$$\left(\frac{\partial U}{\partial v}\right)_S = p \dots \dots \dots (16)$$

On eliminating p from this equation by means of equation (5) we obtain

$$\left(\frac{\partial U}{\partial v}\right)_s = \left(\frac{\partial U}{\partial v}\right)_T - \left(\frac{\partial p}{\partial T}\right)_v. \quad . \quad . \quad . \quad (17)$$

For any state of the substance at the absolute zero of temperature we therefore have

$$\left(\frac{\partial U}{\partial v}\right)_s = \left(\frac{\partial U}{\partial v}\right)_T. \quad . \quad . \quad . \quad . \quad (18)$$

This equation expresses that an adiabatic change at the absolute zero of temperature is not attended by a change in temperature. Hence the adiabatic corresponding to zero entropy in a diagram expressing the relation between v and T lies entirely on the v -axis. This result follows also from the fact that the entropy corresponding to any point in the space enclosed by the positive v and T axes is larger than that corresponding to the point v_0 on the v axis.

7. From the previous Section it follows directly that

$$\left(\frac{\partial v}{\partial T}\right)_s = \infty, \quad . \quad . \quad . \quad . \quad (19)$$

$$\left(\frac{\partial p}{\partial T}\right)_s = \infty, \quad . \quad . \quad . \quad . \quad (20)$$

$$\left(\frac{\partial U}{\partial T}\right)_s = \infty, \quad . \quad . \quad . \quad . \quad (21)$$

for a substance or mixture at the absolute zero of control.

From thermodynamics we have

$$\left(\frac{\partial S}{\partial v}\right)_p = \left(\frac{\partial p}{\partial T}\right)_s. \quad . \quad . \quad . \quad . \quad (22)$$

and

$$\left(\frac{\partial v}{\partial T}\right)_s = -\left(\frac{\partial S}{\partial p}\right)_v, \quad . \quad . \quad . \quad . \quad (23)$$

and hence at the absolute zero of control we also have

$$\left(\frac{\partial S}{\partial v}\right)_p = \infty, \quad . \quad . \quad . \quad . \quad (24)$$

$$\left(\frac{\partial S}{\partial p}\right)_v = -\infty, \quad . \quad . \quad . \quad . \quad (25)$$

8. From equations (14) and (3) we have

$$\left(\frac{\partial p}{\partial T}\right)_v = 0 \quad . \quad . \quad . \quad . \quad . \quad (26)$$

at the absolute zero of control.

9. In general

$$\left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_s + p \left(\frac{\partial v}{\partial T}\right)_s = \left(\frac{\partial S}{\partial T}\right)_s = 0$$

for an adiabatic transformation, which may be written

$$\left(\frac{\partial U}{\partial T}\right)_v + T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_s = 0 \quad . \quad . \quad . \quad (27)$$

by means of equation (5). At the absolute zero of control we may write the equation in the form

$$\infty = \left(\frac{\partial v}{\partial T}\right)_s = - \frac{\left(\frac{\partial U}{\partial T}\right)_v}{T \left(\frac{\partial p}{\partial T}\right)_v} = - \frac{0}{0},$$

according to equations (19), (26), and (2). This equation may be written

$$\infty = \left(\frac{\partial v}{\partial T}\right)_s = - \frac{\left(\frac{\partial^2 U}{\partial T^2}\right)_v}{T \left(\frac{\partial^2 p}{\partial T^2}\right)_v + \left(\frac{\partial p}{\partial T}\right)_v} = - \frac{0}{0},$$

by means of the differential calculus, the right-hand side again assuming a limiting form on account of equations (26) and (9), and the equation $T=0$. This equation may therefore be written

$$\infty = \left(\frac{\partial v}{\partial T}\right)_s = - \frac{\left(\frac{\partial^3 U}{\partial T^3}\right)_v}{2 \left(\frac{\partial^2 p}{\partial T^2}\right)_v + T \left(\frac{\partial^3 p}{\partial T^3}\right)_v},$$

by means of the differential calculus. Now in order that the right-hand side of this equation may be ∞ , we must have

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0, \quad . \quad . \quad . \quad . \quad (28)$$

whatever the value of $\left(\frac{\partial^3 U}{\partial T^3}\right)_v$ may be

This equation and equation (26) are of considerable importance. Every equation of state has to satisfy them, and they are therefore of use to determine the proper form of the equation of state. Evidently van der Waals' equation does not satisfy these equations, and his equation of state has therefore not the fundamentally correct form. It is an important problem to find an equation of state which will satisfy equations (28) and (26).

As an example of the value of these equations in helping to determine the form of the equation of state, let us write it in the form of the series

$$p = A \frac{RT}{v} + \frac{a_1 + a_2 T + a_3 T^2}{v^2} + \frac{b_1 + b_2 T + b_3 T^2}{v^3}, \quad (29)$$

where $A, a_1, a_2, a_3, b_1, b_2, b_3$ are constants. Equations (28), (26), and the equation $p=0$ give

$$0 = a_1 + \frac{b_1}{v_0},$$

$$0 = AR + \frac{a_2}{v_0} + \frac{b_2}{v_0^2},$$

$$0 = a_3 + \frac{b_3}{v_0},$$

taking into account that $T=0$ and $v=v_0$, the conditions under which the quoted equations hold. The foregoing equations express relations between the constants of the equation of state and v_0 .

10. On differentiating equation (5) twice with respect to T at constant volume, it becomes

$$\frac{\partial^3 U}{\partial v \cdot \partial T^2} = \left(\frac{\partial^2 p}{\partial T^2} \right)_v + T \left(\frac{\partial^3 p}{\partial T^3} \right)_v.$$

On taking into account equation (28), that $\left(\frac{\partial^3 p}{\partial T^3} \right)_v$ is not infinite according to the postulate given, and that $T=0$, the equation becomes

$$\frac{\partial^3 U}{\partial v \cdot \partial T^2} = \frac{\partial^2 c_v}{\partial v \cdot \partial T} = 0. \quad (30)$$

If the specific heat is expressed by the general equation (8) it will satisfy the foregoing equation if either

$$\left(\frac{\partial \phi_1}{\partial v} \right)_T = 0 \quad (31)$$

or

$$\left(\frac{\partial \phi_2}{\partial T} \right)_v = 0. \quad (32)$$

Along the same lines it can be shown that

$$\frac{\partial^{3+n}U}{\partial v \cdot \partial T^{2+n}} = \frac{\partial^{2+n}e_v}{\partial v \cdot \partial T^{1+n}} = (1+n) \left(\frac{\partial^{2+n}p}{\partial T^{2+n}} \right)_v, \quad (33)$$

where n can only have positive and zero values, and the right-hand side can be evaluated by means of the equation of state.

11. On differentiating equation (14) with respect to T and taking account of equation (28), we obtain

$$\frac{\partial^2 S}{\partial v \cdot \partial T} = 0, \quad (34)$$

an equation parallel in form to equation (7) when $n=0$.

Again, on differentiating the same equation $1+n$ times with respect to T we obtain

$$\frac{\partial^{2+n}S}{\partial v \cdot \partial T^{1+n}} = \left(\frac{\partial^{2+n}p}{\partial T^{2+n}} \right)_v, \quad (35)$$

where the right-hand side may be evaluated by means of the equation of state.

12. The equation

$$\left(\frac{\partial p}{\partial T} \right)_v = 0$$

given in Section 8 expresses that $\partial p=0$ on increasing the temperature of the substance at constant volume. Since the pressure is initially zero it follows that it remains zero, and in keeping the volume constant we therefore exercise no constraint. This result will therefore also hold if the volume is unrestricted, or

$$\frac{dp}{dT} = 0, \quad (36)$$

the differential coefficient (which is total) applying to a substance under the pressure of its own vapour.

Along the same lines it can be deduced from equation (28) that

$$\frac{d^2 p}{dT^2} = 0. \quad (37)$$

Thus the equation quoted may be written

$$\left(\frac{\partial^2 p}{\partial T^2} \right)_v = \left(\frac{\partial^2 x}{\partial T^2} \right)_v = 0.$$

It expresses that $\partial x=0$ on increasing the temperature of

the substance at constant volume. Since x is initially zero (equation 26) it remains zero, and we are therefore exercising no constraint in keeping the volume constant. Therefore the constraint may be supposed removed, giving

$$\frac{dx}{dT} = 0,$$

and since we have already seen that the volume constraint may be removed from $\left(\frac{\partial p}{\partial T}\right)_v$, or x , we finally obtain equation (37).

The foregoing equations are of considerable importance. The vapour pressure equation of a substance or mixture, which connects the vapour pressure with the temperature, must satisfy them. They evidently express that near the absolute zero of temperature the vapour pressure p is given by

$$p = a_1 T^{2+a_2}, \quad . \quad . \quad . \quad . \quad . \quad (38)$$

where a_1 and a_2 are positive quantities depending only on the nature of the substance. This equation could be tested experimentally by means of a special device for measuring low gaseous pressures, such as the one depending on ionization. Its experimental proof would be direct evidence of the fundamental results established in the previous paper on the basis of thermodynamics.

13. In the previous Section we have seen that, keeping the volume of a substance constant on increasing the temperature by ∂T does not act as a constraint. The unrestricted volume therefore does not change on change of temperature, and we may write

$$\left(\frac{\partial v}{\partial T}\right)_p = 0 \quad . \quad . \quad . \quad . \quad . \quad (39)$$

and

$$\frac{dv}{dT} = 0, \quad . \quad . \quad . \quad . \quad . \quad (40)$$

since p is zero and remains zero on change of temperature.

It was also shown that keeping the volume constant during the change $\partial^2 T$ did not act as a constraint. The volume therefore did not change, and we may write

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

$$\frac{d^2 v}{dT^2} = 0. \quad . \quad . \quad . \quad . \quad . \quad (42)$$

The equation of state of a substance must obey equations (39) and (41); and the equation connecting its volume with the temperature when in contact with its vapour must obey equations (40) and (42). The volume temperature equation will evidently assume the form

$$v = v_0 + b_1 T^{2+b_2} \dots \dots \dots (43)$$

near the absolute zero of temperature, where b_1 and b_2 are positive constants depending only on the nature of the substance or mixture. This equation may be tested experimentally by measuring the expansion with change in temperature of the solidified substance near the absolute zero of temperature.

It may be noted that if p and v can be expanded in powers of T by Taylor's Theorem, as is very likely, a_2 and b_2 in equations (38) and (43) are each equal to unity.

14. For the entropy of a substance in contact with its vapour we may write

$$\frac{dS}{dT} = \left(\frac{\partial S}{\partial v} \right)_T \frac{dv}{dT} + \left(\frac{\partial S}{\partial T} \right)_v.$$

The differential coefficients on the right-hand side are zero according to equations (3), (4), and (40), and hence we have

$$\frac{dS}{dT} = 0. \dots \dots \dots (44)$$

If the condition is imposed that the pressure is to remain constant, the former equation becomes

$$\left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial S}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p + \left(\frac{\partial S}{\partial T} \right)_v.$$

The right-hand side is zero according to equations (3), (4), and (39), and hence we have

$$\left(\frac{\partial S}{\partial T} \right)_p = 0. \dots \dots \dots (45)$$

On differentiating the first equation of this Section totally with respect to T , it becomes

$$\frac{d^2 S}{dT^2} = \frac{d}{dT} \left(\frac{\partial S}{\partial v} \right)_T \frac{dv}{dT} + \left(\frac{\partial S}{\partial v} \right)_T \frac{d^2 v}{dT^2} + \frac{\partial^2 S}{\partial v \cdot \partial T} \frac{dv}{dT} + \left(\frac{\partial^2 S}{\partial T^2} \right)_v.$$

According to equations (40), (42), and (11) this equation

may be written

$$\frac{d^2S}{dT^2} = \left(\frac{\partial^2 S}{\partial T^2} \right)_v = \frac{1}{2} \left(\frac{\partial^3 U}{\partial T^3} \right)_v \quad \dots \quad (46)$$

Similarly it can be shown that

$$\left(\frac{\partial^2 S}{\partial T^2} \right)_p = \frac{1}{2} \left(\frac{\partial^3 U}{\partial T^3} \right)_p \quad \dots \quad (47)$$

15. The change in internal energy of a substance in contact with its vapour is given by

$$\frac{dU}{dT} = \left(\frac{\partial U}{\partial v} \right)_T \frac{dv}{dT} + \left(\frac{\partial U}{\partial T} \right)_v \quad \dots \quad (48)$$

The right-hand side is zero according to equations (1), (2), and (40), and hence we have

$$\frac{dU}{dT} = 0. \quad \dots \quad (49)$$

If the condition is imposed that the pressure is to remain constant, equation (48) becomes

$$\left(\frac{\partial U}{\partial T} \right)_p = \left(\frac{\partial U}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p + \left(\frac{\partial U}{\partial T} \right)_v \quad \dots \quad (50)$$

The right-hand side is zero according to equations (1), (2), and (39), and hence we have

$$\left(\frac{\partial U}{\partial T} \right)_p = 0. \quad \dots \quad (51)$$

The specific heat c_p at constant pressure is given by

$$c_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial v}{\partial T} \right)_p, \quad \dots \quad (52)$$

which becomes

$$c_p = 0 \quad \dots \quad (53)$$

by means of equations (51), (39), and since $p=0$.

The specific heat c of a substance under its vapour pressure is given by

$$c = \frac{dU}{dT} + p \frac{dv}{dT}, \quad \dots \quad (54)$$

which becomes

$$c = 0 \quad \dots \quad (55)$$

by means of equations (49), (40), and since $p=0$.

16. On differentiating equation (48) totally with respect to T it becomes

$$\frac{d^2U}{dT^2} = \frac{d}{dT} \left(\frac{\partial U}{\partial v} \right)_T \frac{dv}{dT} + \left(\frac{\partial U}{\partial v} \right)_T \frac{d^2v}{dT^2} + \frac{\partial^2 U}{\partial v \cdot \partial T} \frac{dv}{dT} + \left(\frac{\partial^2 U}{\partial T^2} \right)_v.$$

The right-hand side is zero according to equations (40), (42), and (9), and hence

$$\frac{d^2U}{dT^2} = 0. \quad . \quad . \quad . \quad . \quad . \quad (56)$$

On differentiating equation (50) with respect to T , keeping the pressure constant, we obtain

$$\left(\frac{\partial^2 U}{\partial T^2} \right)_p = 0 \quad . \quad . \quad . \quad . \quad . \quad (57)$$

according to equations (39), (41), and (9).

Equation (54) on differentiating it totally with respect to T becomes

$$\frac{dc}{dT} = 0, \quad . \quad . \quad . \quad . \quad . \quad (58)$$

taking into account equations (57), (36), and (42).

Equation (52) on differentiating it with respect to T at constant pressure becomes

$$\left(\frac{\partial c_p}{\partial T} \right)_p = 0, \quad . \quad . \quad . \quad . \quad . \quad (59)$$

taking into account equations (57), (26), and (41).

It may be pointed out that the results given in the foregoing Sections, with the exception of those in Sections 1, 4, and 5, cannot be deduced from Nernst's theorem and the third law of thermodynamics, but the general result obtained by the writer is necessary of which they form a part, namely, that the controllable internal energy and entropy of a substance and mixture is zero in the condensed state under the pressure of its vapour at the absolute zero of temperature, and that this zero fulfils the mathematical definition of a minimum according to the differential calculus, which yields equations (1), (2), (3), and (4) on which the deductions made are based. The results in Sections 1, 4, and 5 are deduced directly from well-known thermodynamical formulæ.

The subject may be further developed along similar lines, which will be carried out in subsequent papers.

XXV. *A Distant-reading Instrument for the Measurement of Small Deflections.* By E. F. RELF, A.R.C.Sc., and L. F. G. SIMMONS, M.A., A.R.C.Sc., of the Aerodynamics Department, National Physics Laboratory*.

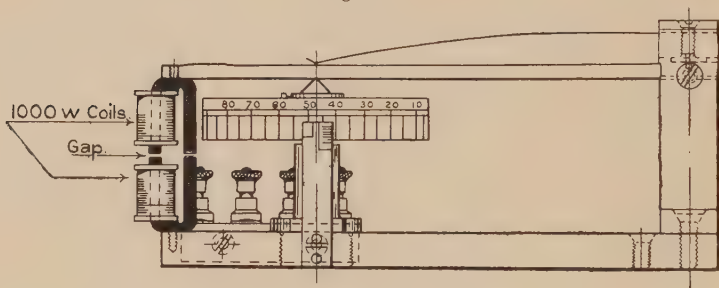
THE apparatus described in this paper was developed in response to a need for an instrument which would indicate at a distance the magnitude of the aerodynamic forces acting on models which were mounted in such a way that direct measurement by balance was impossible, *e. g.* on a whirling arm. The method which has hitherto been used in such cases consists essentially in balancing the force against a calibrated spring, equilibrium of the balance-arm being indicated at a distance by electric contacts. The spring is set to a convenient tension, and the speed of the model through the air varied until balance is obtained. The obvious disadvantage of this method is that it involves access to the model and re-setting of the spring for every reading. The advantage of a method giving, at a distance, a continuous reading proportional to the force acting is obvious, as it would enable a whole series of results at different wind-speeds to be obtained successively and rapidly.

In the search for such a method, various physical properties of materials might conceivably be used to enable the force under measurement to produce an effect at a distance. The most satisfactory method would be one in which an electrical change could be produced without permitting an unduly large movement of the point of application of the force. In America an attempt has been made to use the variation of resistance of a pile of carbon disks compressed by the force. Many difficulties were experienced, and, as far as is known, the only instrument which proved satisfactory was one designed for fairly large forces. An attempt was made at the laboratory to construct a very small carbon pile sensitive to forces of the order 1/100 lb., but did not promise success, as the instrument was found to be very unreliable, the resistance being dependent upon the previous history of the loading to a considerable extent. Piezo-electric phenomena were also considered, but were rejected on the grounds that even if a crystal could be obtained which would give a sufficient change of potential with the small forces involved, the measurement of a small electrostatic potential is difficult and requires very careful insulation, which could not be easily obtained under conditions contemplated.

* Communicated by the Authors.

It was finally decided that the only practical method of any promise was to cause the force to be determined to deflect a very stiff spring, and to measure this deflexion by an electrical method. The apparatus depends upon the change

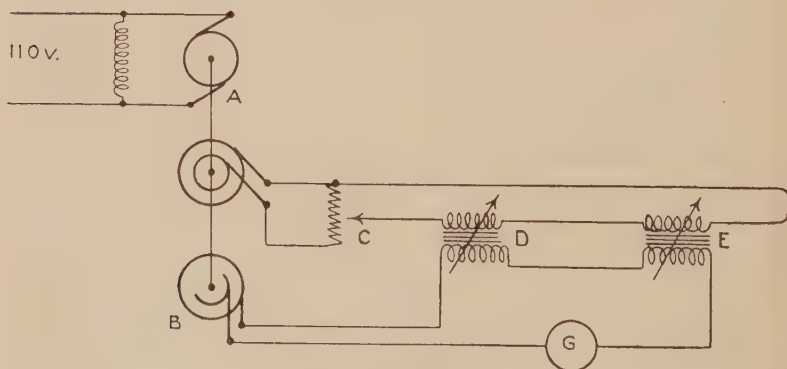
Fig. 1.



Measuring-Gap with Micrometer Adjustment.

in mutual inductance between two coils mounted on an iron core in which there is an air-gap, produced by an alteration in the width of the gap. If two such systems are used, one coil of each being supplied (in series) with alternating current while the other coils are connected so that the induced e.m.f.'s are in opposition, it is evident that a current will flow in the secondary circuit unless the mutual inductances are equal.

Fig. 2.



Circuit Diagram.

The very small alternating currents induced are difficult to measure with accuracy; and even if this could be conveniently done, there is the disadvantage that an alternating current measurement would not indicate which inductance was the greater. The device shown in the circuit diagram (fig. 2)

was accordingly developed so as to permit the use of an ordinary moving-coil galvanometer, and at the same time to indicate the sign of the difference between the gaps. In this figure, A is a rotary converter made by taking two tappings to slip-rings from the armature of a $1/8$ H.P. D.C. motor. The shaft of the motor carries a commutator B, which consists of one complete slip-ring and one half-ring (the motor being a two-pole machine). The brushes on the commutator B are mounted so that they can be rotated about the shaft and locked at any position; thus the commutator can be set to make and break once per revolution at any desired phase-angle. The alternating output of the convertor is taken to a potentiometer C, so that any desired voltage can be applied to the "primary" windings of the two gaps D and E. The "secondaries" of D and E are connected in opposition, and in series with the commutator B and the moving-coil galvanometer G.

The procedure adopted is as follows:—The gaps D and E are set unequal, so that there is a resultant e.m.f. in the secondary circuit, and the phase-angle of the commutator brushes is adjusted to give maximum deflexion of the galvanometer G. The commutator is thus set to make and break when the secondary current is zero, *i. e.* to give half-wave rectification. In practice the gap D is attached to the apparatus whose displacement is to be measured, while E is operated by a micrometer screw. The measuring-gap D is now set at various positions, *e. g.* by the application of suitable known forces to the balance carrying it, and the readings of the micrometer-gap E taken for balance of the galvanometer. Alternatively, E may be fixed and the deflexion of the galvanometer calibrated against force applied to the apparatus at D. The null method is to be preferred, since, if the gaps D and E are magnetically similar, the null method is independent of frequency, and it is not necessary to take any special precautions to keep the speed of the generator A constant.

It is not essential that the phase-angle of the brushes on the commutator B should be set exactly to the correct position for half-wave rectification. The null method is independent of this setting, but the sensitivity of the device is obviously a maximum when half-wave rectification is obtained. In the direct-deflexion method change of this phase-angle will alter the galvanometer current, but the calibration of the whole apparatus is definite for any commutator setting, provided the frequency and applied voltage are kept constant.

Details of the measuring-gap and micrometer are shown in fig. 1. The coils are 1000-ohm bobbins, commonly used for wireless head-phones. With an applied e.m.f. of about 2 volts from the potentiometer C, and using a reflecting galvanometer giving 1 cm. scale deflexion for 10^{-7} amp., a change of 1/10,000 inch in either gap gives a scale deflexion of about 5 millimetres.

Some little difficulty was first experienced with the commutator in the galvanometer circuit. This became heated, and set up a small e.m.f. which disturbed the galvanometer zero. The effect was greatly reduced by lubricating the commutator with oil, and was entirely eliminated by constructing a commutator in which the rings and brushes were cut from the same sheet of metal.

The magnetic force in the measuring-gap is measurable under the conditions of sensitivity described above, but would generally be a very small fraction of the force to be measured. It is eliminated in both the null method and the direct-deflexion method by the process of calibration described above. The apparatus cannot be applied to indicate the zero position of a very sensitive balance, since the magnetic force in the gap tends to reduce the stability of the balance. It must also be remembered that the variation of secondary current with gap is not linear, so that the instrument would indicate an incorrect mean if there were a vibration of considerable amplitude in the measuring-gap. It is possible that the calibration could be made nearly linear over a chosen range by suitably shaping the pole-pieces.

XXVI. *The Physical Form of Ether.* By D. MEKSYN*.

I. INTRODUCTION.

1. *On the Character of the Laws of Ether.*

IT is known that between geometrical propositions there are such as cannot be proved but are to be considered as self-evident: these are the so-called axioms of Geometry.

Theoretical Physics presents a somewhat similar case. Its laws are derived by means of mathematical analysis from data of experimental physics, which in their turn are results of measurements.

* Communicated by Prof. H. Levy, D.Sc.

A necessary condition of every measurement is that the unit shall be smaller than the measured quantity: the smaller the standard of measurement is in comparison with the measured quantity, the more precisely the phenomenon can be described. We can measure an event which lasts a day by a clock which indicates minutes and hours, but we are unable to trace a phenomenon which is changing during a minute by means of a clock which marks hours.

Our standards of measurement are finite pieces of matter—atoms, light-waves, and electrons.

Suppose now that we have to deal with a phenomenon which is changing along a length insignificant in comparison with the size of an electron, or during an interval very small in comparison with the time which light takes to pass the electron. It seems that there is no means at our disposal to describe this phenomenon, unless we succeed in splitting up electrons. When physics reaches this stage, the character of its laws must become changed. Instead of being a science which strives to find out the "substance" of phenomena, it becomes a science of a form of phenomena, a kind of Geometry. This takes place when we are dealing with laws of Ether.

Experimental physics at present does not provide us with the necessary information to find out the substance of Ether, electricity and gravitation, and hence there is no need for it in so far as the explanation of results of measurements is concerned.

This has a bearing on the very startling fact that Einstein applying some general considerations succeeded in giving the laws of electricity and gravitation.

2. Some instances of the Form of Ether.

Let us now consider some instances of these considerations. As we shall see, the mechanical action of Ether is due to a kind of four-dimensional displacement of the medium. We do not know the mechanism of this displacement: how does it come about that matter follows the form of this displacement, or by what means it is generated, spread and kept in the medium. The only assumption is that the medium is continuous and incompressible.

Let us find the law of this displacement if we suppose that it is generated from some centre, that it depends for remote points only upon the distance from this centre, and is derived from a potential. (The latter, it seems, is necessary for the stability of the configuration, § 25.)

The law of continuity of an incompressible medium is

$$\frac{\partial \delta x}{\partial x} + \frac{\partial \delta y}{\partial y} + \frac{\partial \delta z}{\partial z} = 0. \quad . \quad . \quad . \quad (1)$$

Now

$$\delta x = \frac{\partial \phi}{\partial x}, \quad \delta y = \frac{\partial \phi}{\partial y}, \quad \delta z = \frac{\partial \phi}{\partial z};$$

hence from (1) we find

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0. \quad . \quad . \quad . \quad (2)$$

As the phenomenon has a radial symmetry, (2) becomes

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} = 0$$

or

$$\phi = \frac{m}{r}.$$

If the form of Ether is represented by a potential function ϕ , the force is given by

$$\frac{\partial \phi}{\partial r} = -\frac{m}{r^2},$$

or we obtain Newton's and Coulomb's laws.

Let the phenomenon be generated from an infinite straight line, and depend for remote points upon the distance from this line.

For this case (2) becomes

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} = 0$$

or

$$\phi = m l g r,$$

and the force

$$f = \frac{m}{r}.$$

This is the law of gravitation of an infinite material line and the law of a magnetic field of an infinite straight current.

From these instances we see that, whatever may be the cause of a phenomenon, its observed laws are defined by the physical form of the medium, and not by the intrinsic mechanism of phenomena or of the medium undetectable by our measurements.

3. *Ether and Motion.*

In Physics the idea of Ether always comes in connexion with the phenomenon of light or electromagnetic field. It is not considered that the Ether has any bearing on motion of a free material point in space.

Newton's dynamics accepts that a free material point moves in a straight line, because it is the shortest line of the space; it is necessary to apply some force to deflect it from this line because of the law of causality, the force being proportional to some property of a body called its mass, and to the acceleration. The laws of motion centre themselves mainly in the body itself; they are the most simple laws conceivable, but, as a matter of fact, a more detailed examination shows them to be quite incomprehensible.

If a body receives an acceleration, what change has occurred in the interrelation between space and the body? We assume that there is no Ether: the space is void. As the space is quite homogeneous and infinite, and as there is no discrimination between directions or parts of space, there must not be any force applied in order to bring the body from one part of space to another: the law of Motion ought to be according to the law of probability.

We could take up an alternative point of view, and ascribe the laws of Motion to the action of distant masses.

If a material point moves, its distance from distant masses changes, and hence there is a force necessary to produce this change. But here again two cases are possible: either the distant masses are distributed symmetrically in relation to the moving body (then their influence is mutually cancelled and the law of probability persists), or there is no such symmetry (then there must be a marked out direction in which all bodies strive to move, which is contrary to Newton's laws).

It is clear that if a force is necessary to deflect a moving body, it is because motion produces some change in space, and so we come to the conception of Ether.

Ether and Matter (or electrons) are mutually connected parts of one physical system: to every state of matter its state of Ether corresponds; *every Motion of Matter (or electrons) produces a corresponding displacement of Ether.*

It is the latter which defines the laws of Motion of a material body.

Now what is Ether? It will be assumed that free Ether is an absolutely continuous, incompressible, and elastic dynamical substance, *sui generis*, possessing a definite amount of Energy in every unit of volume. It is clear that, whatever the laws of Ether may be, they must be in accordance

with the general laws of equilibrium and Motion of a continuous elastic medium.

From the dynamics of a material point there can be some inferences drawn about deformations of Ether, if the latter is compared with an elastic solid body.

Three kinds of changes can be produced in an elastic solid body without destroying it :—

1. The body can be brought from one state of equilibrium into another. A temporary force is necessary to produce this change, but no force is necessary to keep the body in a state of equilibrium.

2. It can undergo an elastic deformation. Up to a certain limit it is necessary not only to apply a force to bring about this change, but the deformation persists only so long as the force acts, and vanishes together with the force.

3. Above a certain limit the deformation produced in an elastic body persists after the force has been removed.

These three states of a solid body are analogous to three states of Ether.

The first corresponds to a uniform rectilinear motion of a body, the second to an accelerated motion, and the third to electrons and protons, which are permanent four-dimensional deformations of Ether.

4. *The Law of Ether for moving systems.*

Einstein's Principle of Relativity is of great importance to problems connected with moving systems. The idea of this principle is that the laws of Physics are covariant to every system of coordinates, great importance being attached to the use of curvilinear coordinates. It is therefore necessary to inquire as to the bearing which this conception has on the form of Ether. Before it can be done, however, we must make it clear where the kernel of the idea lies.

It seems that the conception of the general Principle of Relativity is either useless or self-contradictory.

As a matter of fact, what is meant by the statement that all laws of Physics are covariant to every system of coordinates? It means that a particular relation, which is the content of a law, does not depend upon a system of coordinates. But, if so, the latter plays only a subsidiary rôle; it is a matter of convenience, and cannot lead us to any new results.

On the other hand, Einstein, using this method, arrived at a new law of gravitation. Hence it appears that the laws of Physics are not covariant to every system of coordinates.

This difficulty is solved as follows :—

The laws of Physics are represented in the four-dimensional Geometry by mixed space-time quantities ; the covariancy of laws of physics relates to these mixed quantities. On the other hand, at the basis of our experimental knowledge lies the intuitive law, that space and time are distinctly separate entities ; our physical instruments are measuring separately the space and the time-parts of the corresponding four-dimensional quantity, which, taken as a whole, has no observable meaning at all.

Take, for instance, the conception of the four-velocity. Its absolute value for *every motion* is equal to

$$\sqrt{\frac{dx^2}{ds^2} + \frac{dy^2}{ds^2} + \frac{dz^2}{ds^2} - \frac{dt^2}{ds^2}} = \sqrt{-1},$$

where

$$ds^2 = dt^2 - dx^2 - dy^2 - dz^2.$$

It consists of two parts : space-part, $\frac{dx}{ds}, \frac{dy}{ds}, \frac{dz}{ds}$, which represents what we grasp to be the velocity of Motion, and the time-part, which is the kinetic energy of Motion. Or take the electromagnetic six-vector. Its invariant value is

$$H_x^2 + H_y^2 + H_z^2 - E_x^2 - E_y^2 - E_z^2.$$

Two quite different electromagnetic phenomena may have an electromagnetic six-vector of the same absolute value ; the latter is not an observable quantity ; only its separate space- and time-parts, the electric and magnetic forces, have to us a physical reality.

Now, if we change a system of coordinates, it leaves invariant only the four-quantity as a whole, but not separately, its space- and time-parts ; hence we see that, in contradistinction to the three-dimensional geometry of space (solid bodies), in the four-dimensional geometry of Ether, although the laws may be covariant, we are not free to use systems of coordinates, because different systems represent quite different phenomena.

Hence, if we accept that the laws of Physics possess a general covariancy, and at the same time we demand that strict physical laws shall exist for moving systems, we come to the conclusion that :

To every moving system, and a field of gravitation, belongs its metric of Ether, which defines the mechanical and electromagnetic properties of the moving system.

II. DYNAMICS OF A MATERIAL POINT.

5. *Motion and the Metric of Ether.*

The problem of Motion consists of two parts :

1. Given the four-dimensional form of Ether (Metric) to find the Motion of a material point in it.
2. Given the motion of a system to find the corresponding metric of Ether, which is produced by this Motion.

We consider in the present investigation only one particular case—when the Force is derived from a Potential.

The solution of the first problem is given by generalization of the principle of Hamilton.

If ds is an element of the four-track, then the Motion of a free material point is given by the geodesic line of Ether (see also § 14),

$$\delta \int ds = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$ds^2 = g_{\mu\nu} dx_\mu dx_\nu.$$

The evaluation of this condition gives the four equations of Motion :

$$\frac{d^2 x_\alpha}{ds^2} + \{\mu\nu, \alpha\} \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} = 0. \quad . \quad . \quad . \quad (2)$$

Comparing (2) with the Classical Laws of Motion, we find that

$$g_{44} = 1 - 2\phi \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(or $g_{44} = 1 - \frac{2\phi}{c^2}$ if c is the velocity of light), where ϕ is the Potential function of the Force on a unit of mass of the Material Point.

The equation (3), together with the condition that

$$g = -1, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

gives to the first approximation the Metric which Ether must possess in order to set the material point in the required motion.

We assume that, conversely, if a system has a Motion which can be produced by a force derived from a potential ϕ , the metric of its Ether observed from a system at rest will be given by (3).

6. The same problem of finding the physical metric of Ether can be attacked more directly.

We find in an invariant form the partial differential equation, which must be satisfied by the potential function ϕ .

Let it be

$$f(\phi, \phi_\alpha, \phi_{\alpha\beta}, g_{\mu\nu} \dots) = 0.$$

From this equation we exclude ϕ and all its derivations: we obtain an equivalent system of equations which must be satisfied by $g_{\mu\nu}$.

Solving them, we find the tensor $g_{\mu\nu}$, which, inserted in (2), gives the Motion of the material point.

We consider a few instances for elucidation of these two methods.

7. Hyperbolic Motion.

1. Let a material point be set in motion under the influence of a constant force.

The potential function is

$$\phi = \alpha x. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If the motion proceeds in the direction of the axis X, g_{44} is given by

$$g_{44} = 1 - \frac{2\alpha x}{c^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Taking the discriminant of the fundamental form to be equal to $-c^2$, we obtain

$$ds^2 = \left(1 - \frac{2\alpha x}{c^2}\right) c^2 dt^2 - dz^2 - dy^2 - \frac{dx^2}{1 - \frac{2\alpha x}{c^2}}. \quad . \quad (7)$$

2. We consider now this problem from the second point of view.

The potential function represents in four-dimensional space a plane; hence its Gaussian curvature, or the Riemann-Christoffel tensor, is equal to zero. This gives us the required condition for $g_{\mu\nu}$.

We can come to the same condition also as follows:—

The differential equation of ϕ is

$$\frac{\partial^2 \phi}{\partial x_\mu \partial x_\nu} = 0,$$

or, in an invariant form,

$$\phi_{\mu\nu} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where subscripts denote covariant differentiation.

Differentiating covariantly (8) once more, we obtain

$$\phi_{\mu\nu\sigma} = 0, \quad (9)$$

whence it follows :

$$\phi_{\mu\nu\sigma} = \phi_{\mu\sigma\nu} + B_{\mu\nu\sigma}^{\epsilon} \phi_{\epsilon} (10)$$

As $\phi_{\mu\nu\sigma} = \phi_{\nu\sigma\mu} = 0$,

(10) becomes

$$B_{\mu\nu\sigma}^{\epsilon} \phi_{\epsilon} = 0. \quad (11)$$

Now, for a suitable system of coordinates the Riemann-Christoffel tensor $B_{\mu\nu\sigma}^{\epsilon}$ becomes a differential equation of the second order in $g_{\mu\nu}$, which in their turn are to the first approximation linear functions of ϕ ; hence $B_{\mu\nu\sigma}^{\epsilon}$ is of the second order of ϕ , and therefore it does not depend upon the particular values of the coefficients α in ϕ . On the other hand, ϕ depends upon them. As they can have arbitrary values, (11) will only be satisfied if

$$B_{\mu\nu\sigma}^{\epsilon} = 0, \quad (12)$$

the above-found condition.

We integrate now (12) for two dimensions, assuming that

$$g = -1.$$

From Differential Geometry we have

$$4\sqrt{g}K + 2\frac{\partial}{\partial x_1}\left(\frac{\frac{\partial g_{44}}{\partial x_1}}{\sqrt{g}}\right) + 2\frac{\partial}{\partial x_4}\left(\frac{\frac{\partial g_{44}}{\partial x_4}}{\sqrt{g}}\right) = 0, \quad . . . (13)$$

where $K = \frac{B_{1212}}{g}$ is the Gaussian curvature.

In our case $K=0$.

If we consider only stationary solutions, (13) becomes

$$\frac{\partial^2 g_{44}}{\partial x_1^2} = 0,$$

or g_{44} is a linear function of X , the above-found result.

8. *Solution of the equations of Motion.*

The motion of a material point is defined from (2), if we insert for $g_{\mu\nu}$ the values given by (7).

The result of these calculations are the two equations of motion :

$$\left. \begin{aligned} \frac{d^2x}{ds^2} + \frac{1}{2} \frac{1}{1-2\alpha x} \left(\frac{dx}{ds} \right)^2 - \alpha &= 0, \\ \frac{d^2t}{ds^2} - \frac{2\alpha}{1-2\alpha x} \frac{dx}{ds} \frac{dt}{ds} &= 0, \end{aligned} \right\} \dots \dots (14)$$

where we take $c=1$ and denote

$$x_1=x, \quad x_4=t.$$

From the second equation (14) we obtain the first integral of Motion :

$$(1-2\alpha x) \frac{dt}{ds} = \text{const.} = p \dots \dots \dots (15)$$

If the initial conditions are $x_0=0$, $v_0=0$, $t_0=0$, then

$$p=1,$$

and from (15) we find

$$v = \sqrt{(1-2\alpha x)^2 - (1-2\alpha x)^3} \dots \dots (16)$$

The maximum velocity of the material point is found from

$$\frac{dv}{dx} = 0 \quad \text{or} \quad 1-2\alpha x = \frac{2}{3};$$

this gives for v

$$v = \frac{2}{3\sqrt{3}} = 0.38.$$

This velocity will be attained at a distance

$$x = \frac{1}{6\alpha}.$$

After this point the velocity will decline, and where

$$1-2\alpha x=0,$$

or at $x = \frac{1}{2\alpha}$, the point will stop.

To find the track we integrate (16), which gives

$$t = \frac{1}{\alpha} \operatorname{tgh}^{-1} \sqrt{2\alpha x},$$

or

$$x = \frac{\operatorname{tgh}^2 \alpha t}{2\alpha} \dots \dots \dots (17)$$

From the first equation (17) we see that the point will stop at

$$t = \infty.$$

9. Harmonic Motion.

This Motion is given by the potential function

$$\phi = \alpha^2 x^2;$$

hence the element of the four-track is

$$ds^2 = (1 + \alpha^2 x^2) dt^2 - dz^2 - dy^2 - \frac{dx^2}{1 + \alpha^2 x^2}. \quad (18)$$

The form of Ether is given by the condition that the Gaussian curvature is constant.

From (13), taking

$$K = \frac{1}{R^2},$$

$$g = -1,$$

we obtain

$$\frac{\partial^2 g_{44}}{\partial x_1^2} = \frac{2}{R},$$

which gives for g_{44} the above-found expression.

The form of Ether is a "sphere" of the radius $\frac{1}{\alpha}$.

The first integral can be obtained from the fourth equation of Motion, and is

$$g_{44} \frac{dt}{ds} = \text{const.} = p. \quad (19)$$

If the initial conditions are

$$t_0 = 0, \quad x = x_0, \quad v = v_0,$$

integrating (19) once more we obtain

$$x = \frac{x_0 \cos \alpha t}{\sqrt{1 + \alpha^2 x_0^2 \sin^2 \alpha t}}. \quad (20)$$

10. Rotation.

We consider another instance of a harmonic Motion—a uniform rotation.

The fundamental quadratic form is

$$ds^2 = (1 + \alpha^2 r^2) dt^2 - \frac{r^2 d\phi^2}{1 + \alpha^2 r^2} - \frac{dr^2}{1 + \alpha^2 r^2} - dz^2, \quad (21)$$

where we have introduced cylindrical coordinates r, ϕ, z, t .

The integration of the second and fourth equations of Motion gives

$$\left. \begin{aligned} g_{22} \frac{d\phi}{ds} &= \frac{r^2}{1 + \alpha^2 r^2} \frac{d\phi}{ds} = h, \\ g_{44} \frac{dt}{ds} &= (1 + \alpha^2 r^2) \frac{dt}{ds} = k. \end{aligned} \right\} \dots (22)$$

Combining (22) and (21), we find the connexion between r and ϕ :

$$\frac{2d\phi}{h} \sqrt{-1} = \frac{(1 + \alpha^2 r^2) d(r^2)}{r^2 \sqrt{\alpha^2 (1 + \alpha^2 h^2) r^4 - (k^2 - 1 - 2h^2 \alpha^2) r^2 + h^2}}. \quad (23)$$

The integration of (23) leads to a transcendental equation in ϕ and r , which cannot be solved in finite terms.

If, however, we take only an approximate solution, this expression becomes simplified, and we obtain

$$\left. \begin{aligned} r &= r_0 [1 - r_0^2 \alpha^2 \sin^2 (1 - \alpha^2 r_0^2) \phi], \\ (1 - \alpha^2 r_0^2) \phi + \frac{r_0^2 \alpha^2 \sin^2 (1 - r_0^2 \alpha^2) \phi}{2} &= \alpha t. \end{aligned} \right\} \quad (24)$$

11. Einstein's Law of Gravitation.

As the last instance we show how Einstein's law of gravitation for free Ether could be derived from Laplace's equation.

In Galilean coordinates the equation of Laplace is

$$\frac{\partial^2 \phi}{\partial t^2} - \frac{\partial^2 \phi}{\partial x^2} - \frac{\partial^2 \phi}{\partial y^2} - \frac{\partial^2 \phi}{\partial z^2} = 0, \quad \dots (25)$$

and in curvilinear coordinates

$$g^{\mu\nu} \phi_{\mu\nu} = 0, \quad \dots (26)$$

where $\phi_{\mu\nu}$ is the second covariant derivative of the scalar potential ϕ , or

$$g_{\mu\nu} \left(\frac{\partial^2 \phi}{\partial x_\mu \partial x_\nu} - \{ \mu\nu, \alpha \} \frac{\partial \phi}{\partial x_\alpha} \right) = 0. \quad \dots (27)$$

To derive Einstein's law we must exclude the first and second derivative of ϕ from (26).

As it is known, it is possible to introduce, without changing the Riemann-Christoffel tensor, such a system of coordinates that for a selected point the first derivatives of $g_{\mu\nu}$ shall vanish, and $\frac{\partial}{\partial x_\alpha} \{ \mu\nu, \sigma \}$ shall be increased by an arbitrary quantity $\alpha^\sigma_{\mu\nu\alpha}$.

For such coordinates (27) becomes

$$g^{\mu\nu} \frac{\partial^2 \phi}{\partial x_\mu \partial x_\nu} = 0. \quad . \quad . \quad . \quad . \quad (28)$$

We prove that if ϕ is a solution of (26), $\frac{\partial \phi}{\partial x_\alpha} = \phi_\alpha$ will also be a solution.

We have for the above-mentioned coordinates

$$g^{\mu\nu}(\phi_\alpha)_{\mu\nu} = g^{\mu\nu} \left(\frac{\partial^2 \phi_\alpha}{\partial x_\mu \partial x_\nu} - \frac{\partial}{\partial x_\mu} \{ \alpha\nu, \epsilon \} \phi_\epsilon \right)$$

as the three-index symbol vanishes.

If ϕ satisfies (26), it follows that

$$g^{\mu\nu} \frac{\partial^2 \phi_\alpha}{\partial x_\mu \partial x_\nu} = g^{\mu\nu} \frac{\partial^3 \phi}{\partial x_\alpha \partial x_\mu \partial x_\nu} = \frac{\partial}{\partial x_\alpha} \left(g^{\mu\nu} \frac{\partial^2 \phi}{\partial x_\mu \partial x_\nu} \right) = 0$$

according to (28) and because $\frac{\partial g^{\mu\nu}}{\partial x_\alpha}$ vanishes.

We can also use the arbitrary quantities $a_{\mu\nu\alpha}^\sigma$ in such manner as to make vanish

$$g^{\mu\nu} \frac{\partial}{\partial x_\mu} \{ \sigma\nu, \epsilon \} \phi_\epsilon$$

(see A. S. Eddington, 'The Mathematical Theory of Relativity,' pp. 78 and 177) ; hence

$$g^{\mu\nu}(\phi_\alpha)_{\mu\nu} = 0. \quad . \quad . \quad . \quad . \quad (29)$$

Now the exclusion of derivatives of ϕ from (26) can be made as follows :—

As ϕ is a scalar, the first two subscripts in $\phi_{\alpha\mu\nu}$ can be interchanged ; hence (29) becomes

$$g^{\mu\nu} \phi_{\mu\alpha\nu} = 0, \quad . \quad . \quad . \quad . \quad (30)$$

or interchanging α and ν , we obtain

$$\left. \begin{aligned} g^{\mu\nu} \phi_{\mu\alpha\nu} &= g^{\mu\nu} (\phi_{\mu\nu\alpha} - B_{\mu\nu\alpha}^\epsilon \phi_\epsilon) \\ &= g^{\mu\nu} \phi_{\mu\nu\alpha} - B_{\alpha\epsilon}^\epsilon \phi_\epsilon. \end{aligned} \right\} \quad . \quad . \quad (31)$$

Remembering that

$$g^{\mu\nu} \phi_{\mu\nu\alpha} = (g^{\mu\nu} \phi_{\mu\nu})_\alpha = 0,$$

we obtain from (31)

$$B_{\alpha\epsilon}^\epsilon \phi_\epsilon = 0. \quad . \quad . \quad . \quad . \quad (32)$$

B_{α}^ϵ depends to the first approximation upon the second

derivatives of $g_{\mu\nu}$, or, what is the same, upon the second derivatives of ϕ , because $g_{\mu\nu}$ are to the first approximation linear functions of ϕ .

Now ϕ_ϵ may include an arbitrary constant which will not be in B_a^ϵ ; therefore, in order to satisfy (32), we must have

$$B_a^\epsilon = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

which is Einstein's law of gravitation.

III. DYNAMICS OF A CONTINUOUS MEDIUM.

12. The Law of Continuity is

$$\left(\rho_0 \frac{dx_\nu}{ds}\right)_\nu = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ρ_0 is the invariant density of the Medium.

We expand (1),

$$\begin{aligned} \left(\rho_0 \frac{dx_\nu}{ds}\right)_\nu &= \frac{\partial}{\partial x_\nu} \left(\rho_0 \frac{dx_\nu}{ds}\right) + \{\epsilon\nu, \nu\} \rho_\epsilon \frac{dx_\epsilon}{ds} \\ &= \frac{\partial}{\partial x_\nu} \left(\rho_0 \frac{dx_\nu}{ds}\right) + \frac{1}{\sqrt{-g}} \frac{\partial \sqrt{-g}}{\partial x_\epsilon} \rho_0 \frac{dx_\epsilon}{ds} \\ &= \frac{1}{\sqrt{-g}} \frac{\partial}{\partial x_\nu} \left(\rho_0 \sqrt{-g} \frac{dx_\nu}{ds}\right) = 0, \end{aligned}$$

which for Galilean coordinates becomes the usual law of continuity.

13. The Law of Motion.

As it is known from the General Theory of Relativity, the law of Motion of a continuous medium is

$$\left(p^{\alpha\nu} + \rho_0 \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds}\right)_\nu = 0, \quad . \quad . \quad . \quad . \quad (2)$$

where $p^{\alpha\nu}$ represents the stress and $\rho_0 \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds}$ the energy tensor of the medium.

Let us find the relation of this law to the law of Motion of a material point in Ether :

$$\frac{d^2 x_\alpha}{ds^2} + \{\mu\nu, \alpha\} \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} = 0. \quad . \quad . \quad . \quad . \quad (3)$$

We denote the left side at (3) by F^α :

$$\frac{d^2 x_\alpha}{ds^2} + \{\mu\nu, \alpha\} \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} = F^\alpha, \quad . \quad . \quad . \quad (3a)$$

and transform it.

We multiply (3a) by $\rho_0 \sqrt{g}$ and transform the first term of the left side

$$\begin{aligned} \sqrt{g} \rho_0 \frac{d^2 x_\alpha}{ds^2} &= \rho_0 \sqrt{g} \frac{\partial}{\partial x_\nu} \left(\frac{dx_\alpha}{ds} \right) \frac{dx_\nu}{ds} \\ &= \frac{\partial}{\partial x_\nu} \left(\rho_0 \sqrt{g} \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds} \right) - \frac{dx_\alpha}{ds} \frac{\partial}{\partial x_\nu} \left(\rho_0 \sqrt{g} \frac{dx_\nu}{ds} \right) \\ &= \frac{\partial}{\partial x_\nu} \left(\rho_0 \sqrt{g} \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds} \right), \quad . \quad . \quad . \quad (4) \end{aligned}$$

as the second term vanishes according to the law of Continuity. Now

$$\begin{aligned} \frac{\partial}{\partial x_\nu} \left(\rho_0 \sqrt{g} \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds} \right) &= \sqrt{g} \frac{\partial}{\partial x_\nu} \left(\rho_0 \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds} \right) + \rho_0 \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds} \frac{\partial \sqrt{g}}{\partial x_\nu} \\ &= \sqrt{g} \frac{\partial}{\partial x_\nu} \left(\rho_0 \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds} \right) + \sqrt{g} \{\nu\mu, \mu\} \rho \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds}. \quad (5) \end{aligned}$$

Combining (5), (4), and (3a), we obtain

$$\left(\rho_0 \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds} \right)_\nu = F^\alpha \rho_0. \quad . \quad . \quad . \quad (6)$$

Combining (6) and (2), we obtain

$$\rho_0 \frac{d^2 x_\alpha}{ds^2} + \rho_0 \{\mu\nu, \alpha\} \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} = -p_\nu^{\alpha\nu}. \quad . \quad . \quad (7)$$

14. Several sequels can be drawn from (7):—

1. If $p_\nu^{\alpha\nu} = 0$, the equation (7) coincides with (3), or, *in order that the Motion shall proceed on the geodesic line of the Medium, it is necessary and sufficient that the stress tensor shall be a self-balanced mechanical system.*

2. We multiply (7) by $g_{\alpha\beta} \frac{dx_\beta}{ds}$ and obtain

$$g_{\alpha\beta} p_\nu^{\alpha\nu} \frac{dx_\beta}{ds} = 0. \quad . \quad . \quad . \quad (8)$$

This is the law of Energy of the Medium. It is equivalent to the fourth law of Motion of (7), which is sometimes wrongly considered in the General Theory of Relativity to be the Law of Continuity.

3. For Ether at rest and at motion

$$p_v^{\alpha\nu} = 0 ;$$

hence an electron is moving in an electromagnetic field at the Geodesic line of Ether.

The Law of Energy (8) is identically satisfied for electromagnetic moving systems.

As is known, the Law of Energy breaks down if we apply the formulæ of the Special Theory of Relativity to an accelerated motion of electrons.

IV. ELECTRODYNAMICS.

15. *The Electromagnetic Equations.*

The application of curvilinear coordinates to four-dimensional space presents a difficulty which does not exist in the case of rectilinear coordinates.

As is known, the Lorentz transformations can be derived from the condition that the expression

$$ds^2 = dx_0^2 + dy_0^2 + dz_0^2 + dt_0^2 \quad . \quad . \quad . \quad (1)$$

can be transformed into

$$ds^2 = dx_1^2 + dy_1^2 + dz_1^2 + dt_1^2.$$

If we apply this method to curvilinear coordinates, we must find such a connexion between Galilean and accelerated systems which transform (1) into

$$ds^2 = g_{\alpha\beta} dx_\alpha dx_\beta \quad . \quad . \quad . \quad (2)$$

It is known from deformation of surfaces, that this is only possible if the Riemann-Christoffel tensor of (2) vanishes, which generally is not the case. Therefore the form of Ether in general is characterized not by a particular system of coordinates, but by the fundamental tensor $g_{\mu\nu}$.

At the basis of Electrodynamics of moving systems we take Maxwell's equations of the General Theory of Relativity, the fundamental tensor $g_{\mu\nu}$ depends upon the motion of the System.

For convenience' sake, we give here these equations.
If the four-potential is

$$k^\mu = F, G, H, \phi, \quad (3)$$

the Electromagnetic Force is given by

$$F_{\mu\nu} = \frac{\partial k_\mu}{\partial x_\nu} - \frac{\partial k_\nu}{\partial x_\mu},$$

$$(F^{\mu\nu})_\nu = I^\mu, \quad (4)$$

where

$$I^\mu = \sigma_x, \sigma_y, \sigma_z, \rho$$

is the stream tensor ; the Mechanical Force is

$$h_\mu = F_{\mu\nu} I^\nu, \quad (5)$$

the energy tensor

$$E_\mu^\nu = -F^{\nu\alpha} F_{\mu\alpha} + \frac{1}{4} g_\mu^\nu F^{\alpha\beta} F_{\alpha\beta}, \quad (6)$$

the connexion between E_μ^ν and h_μ is

$$h_\mu = E_{\mu\nu}^\nu \quad (7)$$

(see A. Einstein, 'Die Grundlage der Allgemeiner Relativitätstheorie,' § 20).

The two fundamental problems of Electrodynamics of moving systems are :

1. To find the motion of an electron in a given Electromagnetic field.
2. To find the Electromagnetic field of a moving system.

16. Motion of Electrons.

We must first make the cause of the mechanical actions of an electric field clear. It greatly resembles the gravitational force, but it is quite a different phenomenon. The mechanical action of a Gravitational field is due to the existing curving of the Ether, which is the physical content of gravitation.

The mechanical action of an electric field is more complicated. The electric field of an electron is self-balanced; therefore, as we shall show later, the Ether of the field is not curved (except for the gravitational effect of its energy), and hence has no mechanical action on the electron itself or on matter which may be in the field.

Now, if the electron is introduced in an external field, the equilibrium is violated; to restore it additional stresses become necessary. They change the electric field of an electron, the external field, and curve the Ether; this evokes the Motion of the electron.

The mechanical force of the field upon the electron is given by (5), where in $F_{\mu\nu}$ ought to be included both the external and the field of the electron. As, however, the latter does not produce a mechanical effect, it can be omitted. The problem of Motion is reduced to the finding of the tensor $g_{\mu\nu}$ corresponding to the mechanical force. If the Force is derived from a potential, the tensor $g_{\mu\nu}$ and the Motion can be obtained by the method given in the dynamics of a material point.

17. *Equilibrium of Ether.*

We consider the state of the inner field of a moving electron.

The Ether must be in equilibrium whether the electron is at rest or in Motion.

In the first case the conditions of equilibrium are

$$\operatorname{div}_\nu E_\mu^\nu = \frac{\partial E_\mu^\nu}{\partial x_\nu} = 0$$

(see D. Meksyn, *Phil. Mag.* 1926, p. 998). The conditions for Motion are

$$E_{\mu\nu}^\nu = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or, expanding (8),

$$\frac{1}{\sqrt{-g}} \frac{\partial}{\partial x_\nu} (E_\mu^\nu \sqrt{-g}) = \frac{1}{2} \frac{\partial g_{\alpha\beta}}{\partial x_\mu} E^{\alpha\beta}. \quad . \quad . \quad (9)$$

The left side represents the divergence of the stress tensor, and is equal to zero if the electron is at rest (or in a uniform rectilinear motion).

If the electron has an accelerated motion, this divergence is balanced by the right side, which represents the mechanical reaction of Ether; it is equal and opposite to the external force acting on the electron.

We take the fundamental form to be

$$ds^2 = \left(1 - \frac{2\phi}{m}\right) dt^2 - \frac{dx^2 + dy^2 + dz^2}{1 - \frac{2\phi}{m}}, \quad . \quad . \quad (10)$$

or to the first approximation

$$g_{11} = g_{22} = g_{33} = -1 - \frac{2\phi}{m},$$

$$g_{44} = 1 - \frac{2\phi}{m}, \quad . \quad , \quad . \quad (11)$$

where m is the mass of the electron, and ϕ is the potential of the external force.

Using (11) and the well-known values of $E^{a\beta}$, we obtain for an electron whose electric field is X, Y, Z ,

$$\frac{1}{2} \frac{\partial g_{a\beta}}{\partial x_\nu} E^{a\beta} = - \frac{(X^2 + Y^2 + Z^2)}{4\pi m} \frac{\partial \phi}{\partial x}.$$

We integrate this expression over the whole field: for hyperbolic motion, as $\frac{\partial \phi}{\partial x}$ is the acceleration it has the same value for the whole field, and hence the required integral will be equal to the first approximation to

$$- \frac{2E^0}{m} \frac{\partial \phi}{\partial x}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where E^0 is the energy of the electron: as, on the other hand, (12) is equal and opposite to the external force $\frac{\partial \phi}{\partial x}$, we obtain

$$m = 2E^0. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If we take the fundamental form to be

$$ds^2 = \left(1 - \frac{2\phi}{m}\right) dt^2 - dy^2 - dz^2 - \frac{dx^2}{1 - \frac{2\phi}{m}},$$

we obtain

$$m = \frac{4}{3}E^0, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

the result given by the Special Theory of Relativity.

18. *An Electron in its own Field.*

We show that the field of an electron exerts no mechanical action upon the electron itself.

As we know, the mechanical force is due to curving of Ether. Therefore we have to prove that no such curving exists in the field, or that $g_{\mu\nu} = \text{const.}$

The equations of equilibrium for rest are

$$\left. \begin{aligned} \frac{\partial E_\nu^\mu}{\partial x_\mu} &= 0, \\ h_\nu &= \frac{\partial E_\nu^\mu}{\partial x_\mu} \end{aligned} \right\}; \quad . \quad . \quad . \quad . \quad . \quad (15)$$

the first equations hold for Ether, the second for the electron.

The corresponding equations of equilibrium for Motion are

$$\left. \begin{aligned} E_{\mu\nu}^{\nu} &= 0, \\ h_{\mu} &= E_{\mu\nu}^{\nu} \end{aligned} \right\} \dots \dots \dots (16)$$

We expand (16),

$$h_{\mu} = \frac{1}{\sqrt{-g}} \frac{\partial}{\partial x_{\nu}} (E_{\mu}^{\nu} \sqrt{-g}) - \frac{1}{2} \frac{\partial g_{\alpha\beta}}{\partial x_{\mu}} E^{\alpha\beta}. \quad (17)$$

Combining (17) with (15), we find for Ether and the electron the same condition of equilibrium,

$$E_{\mu}^{\nu} \frac{1}{\sqrt{-g}} \frac{\partial \sqrt{-g}}{\partial x_{\nu}} = \frac{1}{2} \frac{\partial g_{\alpha\beta}}{\partial x_{\mu}} E^{\alpha\beta}. \quad (18)$$

We take the fundamental form to be

$$ds^2 = g_{44} dx_4^2 - g_{11}(dx_1^2 + dx_2^2 + dx_3^2) \quad (19)$$

with the condition

$$g_{11} g_{44} = 1 \quad (20)$$

Inserting in (18) the values of $g_{\mu\nu}$ from (19) and the well-known values of $E^{\alpha\beta}$, we obtain

$$E_{\mu}^{\nu} \frac{1}{\sqrt{-g_{11}^2}} \frac{\partial \sqrt{-g_{11}^2}}{\partial x_{\nu}} = \frac{X^2 + Y^2 + Z^2}{4} \left(\frac{\partial g_{11}}{\partial x_{\mu}} + \frac{\partial g_{44}}{\partial x_{\mu}} \right). \quad (21)$$

The right side of (21) is equal to the first approximation to zero; hence

$$E_{\mu}^{\nu} \frac{\partial \sqrt{-g_{11}^2}}{\partial x_{\nu}} = 0. \quad (22)$$

It is a system of four equations which defines the

$$\frac{\partial}{\partial x_{\nu}} \sqrt{-g_{11}^2}.$$

As

$$|E_{\mu}^{\nu}| = \left(\frac{X^2 + Y^2 + Z^2}{2} \right)^{\frac{1}{2}},$$

(22) can only be satisfied if $\frac{\partial \sqrt{-g_{11}^2}}{\partial x_{\nu}}$ or $g_{11} = \text{const.}$, and from (20) follows that $g_{44} = \text{const.}$

19. The Field of a moving system.

We have now to consider the second problem of Electrodynamics: to find the Electromagnetic field of a moving system.

For this purpose we must know the metric of the Ether of this system.

We have seen in Dynamics how this can be done.

When we have the tensor $g_{\mu\nu}$, the electromagnetic field is found from (4), § 15, with the additional condition,

$$k_{\mu}^{\mu} = 0. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Combining the two equations of (4), § 15, we obtain k_{μ} from

$$g^{\alpha\beta}(k_{\mu})_{\alpha\beta} = \mathbf{I}_{\mu} - \mathbf{G}_{\mu}^{\epsilon} k_{\epsilon}, \quad . \quad . \quad . \quad . \quad (24)$$

and the electromagnetic tensor $F_{\mu\nu}$ from (4), § 15 (see A. S. Eddington, 'The Mathematical Theory of Relativity,' 1923, p. 175).

20. Lorentz transformations for Hyperbolic Motion.

As we have seen, the problem of finding the field of a moving system is reduced to a solution of a partial differential equation of the second order with variable coefficients.

One case, however, exists where the field can be obtained by a mere transformation of coordinates. This case is analogous to a uniform rectilinear motion.

Let x_{μ}^0 be a Galilean system at rest, and x_{μ} a system in motion. We express x_{μ}^0 as a function of x_{μ} , and insert in

$$ds^2 = dx_4^{02} - dx_1^{02} - dx_2^{02} - dx_3^{02}; \quad . \quad . \quad . \quad (25)$$

the latter must be transformed in

$$ds^2 = g_{\mu\nu} dx_{\mu} dx_{\nu}. \quad . \quad . \quad . \quad . \quad (26)$$

This is possible only if the Riemann-Christoffel tensor of (26) vanishes, which case, as we have seen, corresponds to Hyperbolic Motion.

Let us consider an instance where the system is moving along the axis of X.

We have

$$\begin{aligned} ds^2 &= (1 - 2\alpha x) dt^2 - \frac{dx^2}{1 - 2\alpha x} - dy^2 - dz^2 \\ &= dt^{02} - dx^{02} - dy^{02} - dz^{02}. \quad . \quad . \quad . \quad . \quad (27) \end{aligned}$$

The transformations of coordinates are

$$\begin{aligned} x^c &= - \frac{\sqrt{1 - 2\alpha x}}{\alpha} \cosh \alpha t, & t^0 &= \frac{\sqrt{1 - 2\alpha x}}{\alpha} \sinh \alpha t, \\ y^0 &= y, & z^0 &= z; \quad . \quad . \quad . \quad (28) \end{aligned}$$

and hence

$$\left. \begin{aligned} dx^0 &= \frac{\cosh at}{\sqrt{1-2\alpha x}} dx - \sqrt{1-2\alpha x} \sinh at \cdot dt, \\ dt^0 &= \frac{\sinh at}{\sqrt{1-2\alpha x}} dx + \sqrt{1-2\alpha x} \cosh at \cdot dt. \end{aligned} \right\} \quad (29)$$

These expressions can be confirmed by direct insertion in (27).

21. The Electromagnetic Field of Hyperbolic Motion.

We find the Electromagnetic force from the covariant tensor

$$F_{\mu\nu} = \left. \begin{array}{cccc} 0 & -\gamma & \beta & -X \\ \gamma & 0 & -\alpha & -Y \\ -\beta & \alpha & 0 & -Z \\ X & Y & Z & 0 \end{array} \right\} \quad (30)$$

If the field in a Galilean space at rest is $F_{\mu\nu}^0$, the field of a moving system will be

$$F_{\mu\nu} = \frac{\partial x_a^0}{\partial x_\mu} \frac{\partial x_\beta^0}{\partial x_\nu} F_{\alpha\beta}^0; \quad (31)$$

or, using (29), we obtain

$$X = X^0, \quad Y = \gamma^0 \sqrt{1-2\alpha x} \sinh at + Y^0 \sqrt{1-2\alpha x} \cosh at,$$

$$Z = -\beta^0 \sqrt{1-2\alpha x} \sinh at + Z^0 \sqrt{1-2\alpha x} \cosh at,$$

$$\alpha = \alpha^0, \quad \beta = \frac{\beta^0 \cosh at}{\sqrt{1-2\alpha x}} - \frac{Z^0 \sinh at}{\sqrt{1-2\alpha x}},$$

$$\gamma = \frac{\gamma^0 \cosh at}{\sqrt{1-2\alpha x}} + \frac{Y^0 \sinh at}{\sqrt{1-2\alpha x}}. \quad (32)$$

If the field of an electron at rest is X^0, Y^0, Z^0 , its field in a hyperbolic motion is found from (34) if we put

$$\alpha^0 = \beta^0 = \gamma^0 = 0.$$

The Field is to the first approximation the same as if the electron would move without acceleration.

The Electromagnetic Momentum is equal to

$$G_x = \frac{\beta Z - \gamma Y}{4\pi} = -\frac{Z^{02} + Y^{02}}{4\pi} \sinh at \cosh at$$

and the reaction of the field upon the electron

$$\frac{\partial G_x}{\partial t} = -\frac{Z^{02} + Y^{02}}{4\pi} \alpha,$$

or, integrating through the whole Field, we find the reaction

$$F = -\frac{4}{3} E^0 \alpha,$$

which is, as we have seen, counterbalanced by the mechanical stress in Ether.

IV. ETHER AND MATTER.

22. Elasticity of Ether.

We consider now the last property of Ether—its Elasticity.

Maxwell's Electrodynamics ascribed the Electromagnetic Field to stresses in Ether; they are, however, usually considered as useful mathematical expressions without a physical meaning behind them.

It stands to reason that in a Medium so different from a solid body as Ether, stresses shall exist, because great forces are required in order to produce a small change in a form of a solid body; on the other hand, we can move in Ether without applying any force at all.

It is one of the confusions of our intuitive knowledge.

To bring into play elastic forces of Ether, the latter must be deformed. Not every motion in Ether brings about this change. A uniform motion does not deform Ether at all, and an accelerated motion produces only a comparatively small deformation. On the other hand, no change in form of a solid body is possible without bringing into play its elastic forces.

23. Strains in Ether.

Let u_μ ($\mu=1, 2, 3, 4$) be the relative displacement of Ether: then the Strains are

$$e^{\mu\mu} = \frac{\partial u_\mu}{\partial x_\mu}, \quad e_{\mu\nu} = \frac{1}{2} \left(\frac{\partial u_\nu}{\partial x_\mu} + \frac{\partial u_\mu}{\partial x_\nu} \right). \quad \dots \quad (1)$$

Every displacement can be considered as composed of a displacement which is derived from a potential and a rotation.

As the medium is incompressible, we, adding the four equations (9), obtain

$$\sigma = \frac{1}{3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Let us find the Strains for an electron at rest.

The Stresses are

$$\left. \begin{aligned} X_x &= \frac{1}{8\pi} (X^2 - Y^2 - Z^2), \\ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\ T_t &= -\frac{1}{8\pi} (X^2 + Y^2 + Z^2), \\ X_y &= \frac{1}{4\pi} XY; \end{aligned} \right\} . \quad . \quad . \quad (12)$$

inserting (12) in (9) and using (11), we obtain

$$\left. \begin{aligned} e_{xx} &= \frac{m^2}{12\pi E} \frac{3x^2 - y^2 - z^2}{r^6} = \frac{m}{24\pi E} e'_{xx}, \\ e_{xy} &= \frac{1}{8\pi\mu} XY = \frac{m^2}{8\pi\mu} \frac{xy}{r^6}. \end{aligned} \right\} . \quad . \quad (13)$$

To satisfy the conditions of integrability of the Strains, we must have

$$e_{xy} = \frac{m^2}{8\pi\mu} \frac{xy}{r^6} = \frac{m}{24\pi E} e'_{xy}; \quad . \quad . \quad . \quad (14)$$

whence, using (8), we obtain

$$\mu = \frac{3E}{8}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The Strains are the same as found in § 23.

25. *The Strain-Energy Function of Ether and Stability of Electrons.*

It is known that an elastic medium possesses a Strain-Energy function,

$$\delta W = X_x \delta e_{xx} + Y_y \delta e_{yy} + \dots + 2X_y \delta e_{xy} + \dots, \quad . \quad (16)$$

which is a complete differential.

The inner elastic forces of the medium are derived from a potential,

$$V = \int W dv, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where dv is an element of volume.

In order that the medium shall be stable under the action

of these inner forces, it is necessary and sufficient that V shall be a minimum (see G. Kirchhoff, "Mechanik," Vorlesung 27).

We evaluate the function for three dimensions.

Inserting in (16) the values of e_{xx} , e_{xy} ... from (9, 10), we obtain

$$W = \frac{1}{3E} \{ (X_x + Y_y + Z_z)^2 + 4(X_y^2 + X_z^2 + Y_z^2 - X_x Y_x - X_x Z_x - Y_y Z_y) \}. \quad (18)$$

Using Maxwell's expressions for the Stresses (12), we, from (18), find

$$W = \frac{5}{192\pi^2 E} (X^2 + Y^2 + Z^2)^2. \quad \dots \quad (19)$$

As it is known from Thomson's theorem, the energy

$$\int \frac{X^2 + Y^2 + Z^2}{8\pi} dv$$

of an electrostatic Field

$$X = -\frac{\partial}{\partial x}, \quad Y = -\frac{\partial \phi}{\partial y}$$

($\phi = \text{const.}$ on the surface of conductors),

if the charge remains constant, is less than for any other field; hence the electron is in stable equilibrium (§ 18).

26. The Fundamental Form of the Theory of Relativity.

We derive from these considerations one sequel more.

It is known that, in the fundamental form of the Theory of Relativity,

$$ds^2 = dx^2 + dy^2 + dz^2 - c^2 dt^2; \quad \dots \quad (20)$$

the term of time has an opposite sign from the terms of space. This has a bearing on the Law of Constancy of light-propagation.

We show how this could be understood from the Physical Form of Ether.

We have seen that, when electrons are present, Ether is incompressible in four-dimensional space.

Let us however consider such displacements where Ether remains incompressible in the usual sense or only in space; the necessary condition for this is

$$e_{tt} = 0, \quad \text{or} \quad T_t = \frac{1}{3}(X_x + Y_y + Z_z).$$

For an elastic medium the Laws of small motions are

$$\left. \begin{aligned} (\lambda + \mu) \frac{\partial \Delta}{\partial x} + \mu \nabla^2 u + \rho X &= \rho \frac{\partial^2 u}{\partial t^2} \\ \dots \dots \dots \end{aligned} \right\} \dots \dots (21)$$

(see A. Love, 'The Theory of Elasticity,' 1906, p. 131).

In the case of Ether, ρ is the density of its energy, and the dilatation $\Delta = 0$; hence (21) becomes

$$\frac{3E}{8} \nabla^2 u = \frac{\partial^2 u}{\partial t^2} \dots \dots \dots (22)$$

Now E must be positive (if ρ is positive) in order that the medium shall be stable under the action of its inner forces of Elasticity; hence (22) becomes

$$\nabla^2 u = \frac{1}{c^2} \frac{\partial^2 u}{\partial t^2}, \dots \dots \dots (23)$$

where

$$c^2 = \frac{3E}{8\rho} \dots \dots \dots (24)$$

The Lorentz transformations can be derived from (23) under the condition that this equation must preserve the same form for every rectilinear uniform motion.

It seems that the *negative sign at the time member of (20) is necessary for Stability of Ether.*

The velocity of light-propagation is given from (24):

$$c = \sqrt{\frac{3E}{8\rho}} \dots \dots \dots (25)$$

27. Gravitation and the Electrostatic Field of Protons.

The best way of understanding the mutual relation between Electricity and Gravitation (or Motion) is a comparison of Ether with a solid elastic body.

Under the influence of external forces there arise in a solid body two internally-connected phenomena: Elastic stresses and a corresponding change of form.

Ether represents an analogous case where stresses are observed as an electromagnetic field, and a corresponding displacement as gravitation (or mechanical force).

Gravitation and Electricity are two sides of one and the same state of Ether. Electromagnetic Energy must produce a mechanical displacement of Ether or have a

gravitational mass, and, conversely, every mechanical displacement of Ether (Gravitation and Motion) must be accompanied by Electromagnetic stresses.

This explains the influence of Motion and Gravitation upon an Electromagnetic Field, and throws light upon the nature of the Electrostatic field of protons.

As we shall see, it is entirely due to the gravitation of protons and not to their charge.

We know that the Electromagnetic four-potential k_μ of every field satisfies the equations (23), (24), § 19 :

$$k_\mu^\mu = 0, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$g^{\alpha\beta}(k_\mu)_{\beta\alpha} = I_\mu - G_\mu^\alpha k_\alpha. \quad . \quad . \quad . \quad . \quad (27)$$

We integrate (27) for a proton under the assumption that it has no charge, or $I_\mu = 0$.

From the Theory of Gravitation we have

$$G^{\mu\nu} = -8\pi(T^{\mu\nu} - \frac{1}{2}g^{\mu\nu}T), \quad . \quad . \quad . \quad . \quad (28)$$

where

$$T^{\mu\nu} = \rho_0 \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} \quad \text{and} \quad G = 8\pi T = 8\pi\rho_0; \quad . \quad (29)$$

hence

$$G^{\mu\nu} = -8\pi \left(\rho_0 \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} - \frac{1}{2}g^{\mu\nu}\rho_0 \right). \quad . \quad . \quad (30)$$

For Matter at rest, to the first approximation,

$$G_\mu^\nu = 4\pi\rho_0 \quad \text{if} \quad \mu = \nu = 1, 2, 3; \quad . \quad . \quad (31)$$

for $\mu = \nu = 4$,

$$G_4^4 = -4\pi\rho_0, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$\text{and} \quad G_\mu^\nu = 0 \quad \text{if} \quad \mu \neq \nu.$$

For a stationary field, (27) becomes

$$\nabla^2 k_\mu = G_\mu^\epsilon k_\epsilon, \quad . \quad . \quad . \quad . \quad . \quad (33)$$

or

$$\nabla^2 k_\mu = 4\pi\rho_0 k_\mu \quad \text{for} \quad \mu = 1, 2, 3 \quad . \quad . \quad (34)$$

and

$$\nabla^2 k_4 = -4\pi\rho_0 k_4 \quad \text{for} \quad \mu = 4. \quad . \quad . \quad . \quad (35)$$

In the field (34) and (35) are the usual Laplace's equation,

$$\nabla^2 k_\mu = 0. \quad . \quad . \quad . \quad . \quad (36)$$

The solution of (36) for the field is

$$k_\mu = \frac{a_\mu}{r}.$$

300 Dr. Ferguson and Mr. I. Vogel on the Calculation of
Using (26), we obtain

$$a_{\mu} = 0 \quad \text{for} \quad \mu = 1, 2, 3,$$

or the field is purely electrostatic.

We integrate (35) for a particular case of a radial symmetry.

For the field

$$k_4 = \frac{e}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

in the inner of the proton, (35) becomes

$$\frac{\partial^2 k_4}{\partial r^2} + \frac{2}{r} \frac{\partial k_4}{\partial r} = -4\pi\rho_0 k_4$$

or

$$\frac{\partial^2 (k_4 r)}{\partial r^2} = -4\pi\rho_0 (k_4 r),$$

the solution of which is

$$k_4 = \frac{A \sin \sqrt{4\pi\rho_0} \cdot r + B \cos \sqrt{4\pi\rho_0} \cdot r}{r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

From the condition that k_4 must be finite, we obtain from (38)

$$k_4 = \frac{A \sin \sqrt{4\pi\rho_0} \cdot r}{r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

At the surface of the proton, (37) and (39) must be equal: this defines A.

We see that, in so far as the outer field of the Proton is concerned, it will be identical with the field of an electron.

XXVII. *The Calculation of the Equivalent Conductivity of Strong Electrolytes at Infinite Dilution.*—Part I. *Aqueous Solutions.* (iii.) *The Mobilities of the Hydrogen and the Hydroxyl Ions.* By ALLAN FERGUSON, M.A., D.Sc., and ISRAEL VOGEL, M.Sc., D.I.C.*

(a) *The Hydrogen Ion.*

ALTHOUGH the problem of the determination of the mobility of the hydrogen ion at infinite dilution has occupied the attention of investigators for about the last forty years (for complete bibliography see Walden, 'Das Leitvermögen der Lösungen,' 1924; also Parker, J. Amer. Chem. Soc. 1923, xlv. p. 2017), it cannot be said that a

* Communicated by the Authors.

satisfactory value has yet been attained. The accurate measurements of Kraus and Parker (J. Amer. Chem. Soc. 1922, xlv. p. 2429; 1923, xlv. p. 2029) on iodic acid, and of Parker (*ibid.* 1923, xlv. p. 2017) on hydrochloric acid, provide the most reliable data so far published for the calculation of this important constant.

The conductance at infinite dilution for these two acids has now been calculated by the authors' method (Part I. Phil. Mag. 1925, l. p. 971), and the results are shown in Tables I. and II. below.

TABLE I.
Hydrochloric Acid, 25° C.
 $\Lambda_0 = \Lambda + 3061.9 C^{0.96716}$.

C.	Λ .	Λ_0 .
5.0×10^{-5}	425.49	425.70
1.0×10^{-4}	425.29	425.70
2.0×10^{-4}	424.88	425.69
3.0×10^{-4}	424.48	425.68
4.0×10^{-4}	424.08	425.67
5.0×10^{-4}	423.68	425.65
6.0×10^{-4}	423.30	425.65
7.0×10^{-4}	422.93	425.65
8.0×10^{-4}	422.60	425.70
Mean		425.68

TABLE II.
Iodic Acid, 25° C.
 $\Lambda_0 = \Lambda + 4140.8 C^{0.96866}$.

C.	Λ .	Λ_0 .
5.0×10^{-5}	389.28	389.56
6.0×10^{-5}	389.23	389.56
7.0×10^{-5}	389.17	389.56
8.0×10^{-5}	389.12	389.56
9.0×10^{-5}	389.06	389.56
1.0×10^{-4}	389.01	389.56
2.0×10^{-4}	388.47	389.55
3.0×10^{-4}	387.93	389.54
4.0×10^{-4}	387.40	389.55
5.0×10^{-4}	386.88	389.51
6.0×10^{-4}	386.36	389.50
7.0×10^{-4}	385.86	389.50
8.0×10^{-4}	385.38	389.52
9.0×10^{-4}	384.92	389.56
$\times 10^{-3}$	384.48	389.52
Mean		389.54

It will be seen that the consistency of Λ_0 for hydrochloric acid over the range 0.00005 N to 0.0008 N and of iodic acid from 0.00005 N to 0.001 N leaves little to be desired. The values of both B and n in the equation $\Lambda_0 = \Lambda + BC^n$ are of interest. B is very much larger than that deduced for salts (*cf.* Part I., §§ (i.) & (ii.) of this series), while n approaches unity. It is also of interest to note that the values of Λ_0 deduced by Kraus and Parker (*loc. cit.*) for iodic acid (389.55) and by Parker (*loc. cit.*) for hydrochloric acid (425.69) are in excellent agreement with the mean value calculated by the present authors.

Having deduced Λ_0 for these acids, the mobility of the hydrogen ion at 25° may now be computed. Unfortunately, no accurate measurements of the conductivities of aqueous iodate solutions at 25° are at present available, and hence the mobility of the iodate ion and therefore of the hydrogen ion cannot be directly calculated. The mobility (μ_0) of the chlorine ion has, however, been computed by the present writers (Part I., § (ii.) *loc. cit.*), and subtracting this value (76.63) from the conductance at infinite dilution for hydrochloric acid (425.68), the value 349.05 is obtained for the mobility of the hydrogen ion at 25°. The mobility of the iodate ion at 25° is accordingly 389.54—349.05, *i. e.* 40.49. Kraus and Parker (*loc. cit.*) deduced 349.93 from the iodic acid measurements, while Parker (*loc. cit.*) obtained 349.89 from the data on hydrochloric acid, the final value for the mobility of the hydrogen ion at 25° accepted by Parker being 349.89 ± 0.05 , which he regarded as a *minimum value*.

It must, however, be noted that Kraus and Parker assume the value of μ_0 for the chlorine ion at 25° to be 75.8 (Noyes and Falk, J. Amer. Chem. Soc. 1912, xxxiv. p. 479), a value which differs by more than 1 per cent. from the value (76.67) calculated by the present writers from the conductivity measurements of Lorenz and Michael (*Z. anorg. Chem.* 1921, cxvi. p. 161), the most accurate data for aqueous salt solutions at 25° at present available. Further, in deducing μ_0 for the hydrogen ion at 25° from Λ_0 of iodic acid, they assume that the ratio of the conductances at 25° and at 18° of approximately 0.001 N solutions of potassium iodate is equal to the ratio of the conductances at infinite dilution at these two temperatures. By applying this assumption, Kraus and Parker calculate the value of Λ_0 for potassium iodate at 25°. Here, again, data differing from those at which we have arrived are employed; Λ_0 at 18° for potassium iodate is taken as 98.5 (Noyes and Falk, *loc. cit.*)

(*cf.* Ferguson and Vogel, Part I. *loc. cit.*, 98·54), whilst μ_0 for the potassium ion at 25° is assumed to be 74·8 (Noyes and Falk, *loc. cit.*), the value deduced by the authors (*cf.* Part I., § (ii.) this Journal, p. 233) being 75·63 at 25°.

It was thought important to test this assumption of proportionality, and it seemed that some light could be thrown on the validity of the assumption by applying it to two salts closely related to potassium iodate. The data employed were those of Kohlrausch and Maltby (18°) and of Lorenz and Michael (25°); Λ_0 has already been calculated (*cf.* Part I., §§ (ii.) & (iii.)). The results are given in Table III.

TABLE III.

	$18^\circ\Lambda_{0\cdot001\text{ N.}}$	$18^\circ\Lambda_0$	$25^\circ\Lambda_{0\cdot001\text{ N.}}$	$25^\circ\Lambda_0$	$\frac{25^\circ\Lambda_{0\cdot001\text{ N.}}}{18^\circ\Lambda_{0\cdot001\text{ N.}}}$	$\frac{25^\circ\Lambda_0}{18^\circ\Lambda_0}$
KCl	127·34	130·04	147·80	152·26	1·1607	1·1709
NaCl ...	106·49	109·02	124·55	128·05	1·1696	1·1746

The reason for this discrepancy is not far to seek. From the two equations,

$$25^\circ\Lambda_0 = 25^\circ\Lambda + B(0\cdot001)^n$$

and

$$18^\circ\Lambda_0 = 18^\circ\Lambda + B_1(0\cdot001)^{n_1},$$

we have

$$\frac{25^\circ\Lambda_0}{18^\circ\Lambda_0} = \frac{25^\circ\Lambda + B(0\cdot001)^n}{18^\circ\Lambda + B_1(0\cdot001)^{n_1}},$$

and the ratio used by Kraus and Parker to obtain $25^\circ\Lambda_0$ is obtained by neglecting the "B" terms in the dilution equation. Inspection of the tables showing the values of B and n (Part I., §§ (i.) & (ii.) of this series) will show that the order of magnitude of these constants is such that their neglect, even for a concentration of approximately 0·001 N, is likely to introduce appreciable errors.

(b) The Hydroxyl Ion.

The difficulties inherent in the accurate measurement of the conductivities of aqueous solutions of the so-called strong bases have doubtless been responsible for the comparative scarcity of conductivity data in the field (*cf.* Ostwald, *J. prakt. Chem.* 1886, xxxiii. p. 352; 1887, xxxv. p. 112; Bredig, *Z. phys. Chem.* 1894, xiii. p. 289; Winkelblech, *ibid.* 1901, xxvi. p. 428; Calvert, *ibid.* 1901, xxxviii. p. 530; Jones, *Am. Chem. J.* 1901, xxvi. p. 428; Bousfield and Lowry, *Phil. Trans.* 1905, cciv. p. 292; Noyes, *Publ. Carnegie Inst.* 1907, no. 63, p. 262; Frary and Nietz, *J. Amer.*

Chem. Soc. 1915, xxxvii. p. 2263). The only fairly reliable measurements appear to be those of Raikes, Yorke, and Ewart (J. Chem. Soc. 1926, cxxviii. p. 635) on sodium hydroxide solutions at 10°C and 18°C. Their results, however, are not expressed in the generally accepted manner, viz., conductivities at round concentrations, and in order to utilize them in the calculation of the mobility of the hydroxyl ion at infinite dilution, the conductances at round concentration were interpolated from a large scale conductance-concentration graph. While a fairly good curve could be put through the conductance values at 18°, we were unable to do so for the data at 10°.

The conductivity at infinite dilution has been calculated by the authors' method (this Journal, 1925, l. p. 971), and the results are shown in column 3 of Table IV. below. For purposes of comparison, the values of Λ_0 over the same range of concentration computed from the equation

$$\Lambda_0 = \Lambda + 75.7 C^{0.5000}$$

deduced by Raikes, Yorke, and Ewart (*loc. cit.*) are included in the Table.

TABLE IV.

C.	Λ	$\Lambda_0 = \Lambda + 64.4 C^{0.4087}$	$\Lambda_0 = \Lambda + 75.7 C^{0.5000}$
1.0×10^{-3}	215.1	218.9	217.5
2.0×10^{-3}	213.9	218.9	217.3
4.0×10^{-3}	212.1	218.9	216.9
5.0×10^{-3}	211.5	218.9	216.8
8.0×10^{-3}	210.0	218.9	216.8
1.0×10^{-2}	209.3	219.1	216.9

It will be seen that while Λ_0 as deduced by the present authors is constant over the range 0.001—0.01 normal, the values computed from the square root formula show a marked increase at low concentrations. These deviations illustrate clearly the superiority of the general formula

$$\Lambda_0 = \Lambda + BC^n$$

over the very widely-used square root formula.

We arrive thus at the number 218.9 as the most probable value for the conductivity at infinite dilution. The mean value deduced by Raikes, Yorke, and Ewart was 217.0.

In the calculation of the mobility of the hydroxyl ion these authors assume two values for the mobility of the sodium ion at 18°, viz., 43.4 (Noyes and Falk, J. Amer. Chem. Soc. 1912, xxxiv. p. 479) and 43.23 (Washburn, *ibid.* 1918, xl. p. 158) leading to the values 173.6 and 173.8 respectively for the conductance of the hydroxyl ion at infinite

dilution at 18° . If we assume as the most probable value for the mobility of the sodium ion at 18° the value 43.48 deduced in Part I., § (i.) of this series of researches, we find that the conductance of the hydroxyl ion at infinite dilution is $218.9 - 43.5$, i. e. 175.4, a value differing very appreciably from that calculated by Raikes, Yorke, and Ewart.

Summary.

The most probable values for the conductance at infinite dilution of the hydrogen ion at 25° and of the hydroxyl ion at 18° , deduced by the authors' method (Phil. Mag. 1925, l. p. 971), are 349.05 and 175.4 respectively.

One of the authors (I. V.) is indebted to the Trustees of the Dixon Fund for a grant with the aid of which part of the expenses of this investigation has been met.

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XXVIII. *On the Control of the Frequency of Flashing of a Neon Tube by a Maintained Mechanical Vibrator.* By W. A. LEYSHON, *Ph.D.**

[Plates III.-V.]

CONTENTS.

Section 1. Introduction.

- „ 2. Theory.
- „ 3. Experimental Verification of Theory.
- „ 4. Conclusion.

SECTION 1.—*Introduction.*

THE phenomena which accompany the introduction of an alternating voltage into a circuit maintained in electrical vibration, the periodicity of the undisturbed vibration being equal, or nearly equal, to that of the introduced voltage, have attracted much attention, and have, in particular instances, been considered both theoretically and practically.

If an electric oscillatory circuit is coupled with another maintained by a triode, the well-known “Ziehens” effect is

* Communicated by the Author.

produced on varying the electric constants of the coupled circuit in a suitable manner. The theory of this effect was given for the case of varying inductance by Townsend¹; a general discussion of the problem later by Möller²; Albersheim³ has collected together the published data and theory on this subject.

Butterworth⁴ showed that a mechanical vibrator maintained electrically could, in regard to its reaction on the electrical maintaining system, be replaced by an equivalent electric circuit. He used this theorem in explaining the maintenance of a tuning-fork by a triode^{5, 5A}. Hodgkinson⁶ has also discussed this and similar problems mathematically. Dye used Butterworth's method in a theoretical and experimental study of quartz resonators⁷.

The effect on a triode-maintained oscillatory circuit of the introduction of an alternating voltage of a frequency differing little or not at all from the frequency of the undisturbed vibration, this alternating voltage being derived from a second triode-maintained circuit, has been studied experimentally by Vincent⁸, Appleton⁹, the present writer¹⁰, and others^{11, 12, 13}. Appleton discussed the matter theoretically, and applied his solution of the problem to the case of the reception of wireless signals by an oscillating triode. Recently van der Pol¹⁴ has given a very complete theoretical treatment of the latter problem.

It appears that in all these cases the frequency of vibration of the system as a whole tends to become equal to that of the added voltage, even though the frequency of the undisturbed system may differ quite appreciably from this.

The present paper is concerned with the maintenance of a mechanical vibrator by means of a flashing neon tube. The now well-known circuit for producing flashes was first described, and the simple theory of the circuit given, by Pearson and Anson¹⁵. The control of the frequency of flashing of such a circuit by the introduction of an additional alternating voltage has been mentioned by Bedell and Reich¹⁶ in an application of the circuit for the production of a linear time-base in oscillograph records.

Dye has introduced an alternating voltage derived from a tuning-fork-triode circuit into an Abraham-Bloch multivibrator circuit for control of frequency in his standard multivibrator wavemeter¹⁷. The theory of the multivibrator circuit has been recently given by van der Pol in his paper on Relaxation Oscillations¹⁸.

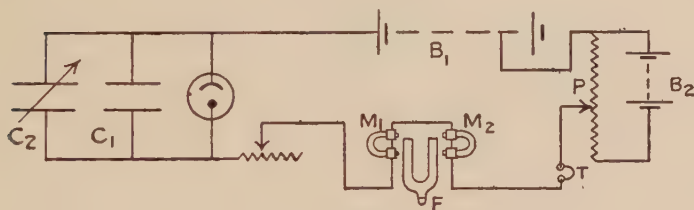
Some direct methods of control of frequency of circuits such as that of the flashing neon tube or the multivibrator

were described in a recent paper in the 'Electrician' ¹⁹; the neon-tube tuning-fork circuit in particular was shown working at the Royal Society Conversazione on June 16th, 1926.

A diagram of the experimental circuit is reproduced in fig. 1.

The electrical vibration in the condenser-neon-tube circuit is very rich in harmonics, since it consists of current impulses of short duration followed by no-current intervals of much longer duration. By means of the tuning-fork the frequency of flashing is kept very nearly constant. Thus the apparatus

Fig. 1.



- B_1, B_2 batteries.
 P potential divider.
 C_1 fixed condenser.
 C_2 variable condenser.
 M_1, M_2 telephone magnets.
 T headphones.

has similar electrical properties to that of the tuning-fork-controlled multivibrator, as described by Dye, but it is of much simpler construction than the latter; the variation with time of the gas-content of the present commercial type of neon tube is a disadvantage, but this difficulty may be overcome in the future ²⁰.

An elementary theory of the action of the tuning-fork in the circuit is developed in the next Section; experimental verifications of the theory are described in Section 3.

SECTION 2.—Theory.

It is first supposed that a sinusoidal voltage of constant amplitude and frequency is introduced into the neon-tube circuit. The differential equation for the circuit is then solved; suitable modifications of the solution are made in order that the introduced voltage may be considered to be due to the motion of the maintained tuning-fork reacting electromagnetically on the circuit.

In the following it is assumed that

- (1) For slow rates of flashing the time of a complete cycle of operations does not differ appreciably from that of a dark period—*i. e.* the flash is regarded as instantaneous.
- (2) The voltage induced in the neon-tube circuit by the tuning-fork at any instant is proportional to the velocity of the prongs at that instant.

The maximum induced voltage during one particular vibration is proportional to the amplitude of vibration of the tuning-fork.

- (3) The work done against dissipative forces during a complete vibration of the tuning-fork is proportional to the square of the amplitude of that vibration. (Frictional force proportional to velocity.)
- (4) The attracting force acting on the prongs of the fork due to the current in the neon-tube circuit is proportional to the current flowing in that circuit at the instant considered.
- (5) The frequency of vibration of the tuning-fork is not affected to an appreciable extent throughout the range of its maintenance, and its motion is a S.H.M.

In a particular cycle of operations, let

v_0 = amplitude of added sinusoidal voltage ;

$w = \frac{2\pi}{T}$, where T = periodic time of vibration of fork ;

t = time which has elapsed since the beginning of the dark period ;

$\phi = \frac{2\pi t'}{T}$, where t' is the interval of time measured from the instant when the fork passes through its position of zero displacement moving towards the attracting coils to the beginning of a dark period.

Then $v_0 \cos (wt + \phi)$ is the actual voltage introduced at a particular instant of time when t seconds have elapsed since the beginning of a dark period.

The equations for the circuit are then

$$B - V - v_0 \cos (wt + \phi) - Ri - L \frac{di}{dt} = 0, \quad \dots (1)$$

$$\left. \begin{aligned} \int_0^t i \cdot dt &= C(V - V_1), \\ \int_0^T i \cdot dt &= C(V_2 - V_1), \end{aligned} \right\} \dots (2)$$

$$\text{or} \quad i = C \cdot \frac{dV}{dt},$$

where B = battery voltage, V = condenser voltage = voltage across lamp at time t ;

C = capacity of condenser + neon-lamp electrodes;

R = resistance in series with lamp—including resistance of tuning-fork coils;

L = inductance of tuning-fork coils (supposed constant);

V_1 = lower critical voltage of lamp;

V_2 = upper " " of lamp;

i = current flowing in the resistance R

[it is supposed that no current flows through the lamp except during the bright period—considered infinitely short in duration].

The differential equation obtained from (1) and (2) is

$$\frac{i}{C} + R \cdot \frac{di}{dt} + L \cdot \frac{di^2}{dt^2} = wv_0 \sin (wt + \phi) \quad . \quad . \quad (3)$$

or

$$\left(\frac{1}{C} + RD + LD^2 \right) i = wv_0 \sin (wt + \phi),$$

where $D = \frac{d}{dt}$.

The solution of this is

$$Ri = A_1 e^{\alpha t} + A_2 e^{\beta t} + \frac{(1 - LCw^2)wRCv_0 \sin (wt + \phi) - w^2 C^2 R^2 v_0 \cos (wt + \phi)}{(1 - LCw^2)^2 + w^2 C^2 R^2}, \quad . \quad . \quad . \quad (4)$$

$$\text{where } \alpha = -\frac{R}{2L} + \sqrt{\frac{R^2}{4L^2} - \frac{1}{LC}}$$

$$\text{or } \alpha = -\frac{R}{2L} \left\{ 1 - \left(1 - \frac{4L}{CR^2} \right)^{\frac{1}{2}} \right\},$$

$$\beta = -\frac{R}{2L} - \sqrt{\frac{R^2}{4L^2} - \frac{1}{LC}}$$

$$\text{or } \beta = -\frac{R}{2L} \left\{ 1 + \left(1 - \frac{4L}{CR^2} \right)^{\frac{1}{2}} \right\},$$

A_1, A_2 are constants determined by setting

$$i = \frac{B - V_1 - v_0 \cos \phi}{R}, \quad \frac{di}{dt} = 0 \quad \text{when } t = 0.$$

* Actually, at the beginning of a dark period $i < \frac{B_1 - V_1 - v \cos \phi}{R}$ owing to the presence of inductance in the circuit.

The equation may be written

$$\begin{aligned}
 Ri = & + \frac{1}{1 - \frac{\alpha}{\beta}} \left[B - V_1 - v_0 Q \left(1 - LCw^2 - \frac{w^2 CR}{\beta} \right) \right] e^{\alpha t} \\
 & + \frac{1}{1 - \frac{\beta}{\alpha}} \left[B - V_1 - v_0 Q \left(1 - LCw^2 - \frac{w^2 CR}{\alpha} \right) \right] e^{\beta t} \\
 & + \frac{(1 - LCw^2)wRCv_0 \sin (wt + \phi) - w^2 C^2 R^2 v_0 \cos (wt + \phi)}{(1 - LCw^2)^2 + w^2 C^2 R^2}, \quad \dots \quad (5)
 \end{aligned}$$

where
$$Q = \frac{(1 - LCw^2) \cos \phi + wCR \sin \phi}{(1 - LCw^2)^2 + w^2 C^2 R^2}.$$

It is seen that the second term quickly becomes negligible if $\frac{L}{CR^2}$ is small and $\therefore \frac{R}{L} \gg \frac{1}{CR}$, which was the case in the experiments to be described. Also, if L is negligibly small, the equation becomes

$$Ri = (B - V_1 - v_0 Q') e^{-t/CR} + \frac{wCRv_0 \sin (wt + \phi) - w^2 C^2 R^2 v_0 \cos (wt + \phi)}{1 + w^2 C^2 R^2}, \quad (6)$$

where
$$Q' = \frac{\cos \phi + wCR \sin \phi}{1 + w^2 C^2 R^2}.$$

This is the solution of the differential equation :

$$\frac{i}{c} + R \cdot \frac{di}{dt} = wv_0 \sin (wt + \phi). \quad \dots \quad (7)$$

If, in equation (6), v_0 is made equal to zero, the equation for i becomes

$$Ri = (B - V_1) e^{-t/CR} \quad \dots \quad (8)$$

—the well-known equation for the charging current in an ordinary “flashing” circuit.

From equation (5) the relation between condenser voltage and time is found, remembering that

$$\frac{1}{c} \int_0^t i \cdot dt = V - V_1.$$

We have

$$V - V_1 = K_1(1 - e^{\alpha t}) + K_2(1 - e^{\beta t}) - v_0 P + v_0 Q, \quad \dots \quad (9)$$

where P is the same function of $(wt + \phi)$ as Q is of ϕ , and

$$K_1 = -\frac{A_1}{\alpha RC}$$

$$= -\frac{1}{\alpha RC\left(1 - \frac{\alpha}{\beta}\right)} \left[B - V_1 - v_0 Q \left(1 - LCw^2 - \frac{w^2 CR}{\beta} \right) \right],$$

$$K_2 = -\frac{A_2}{\beta RC}$$

$$= -\frac{1}{\beta RC\left(1 - \frac{\beta}{\alpha}\right)} \left[B - V_1 - v_0 Q \left(1 - LCw^2 - \frac{w^2 CR}{\alpha} \right) \right];$$

whence

$$V_2 - V_1 = K_1(1 - e^{\alpha T}) + K_2(1 - e^{\beta T}), \quad . \quad . \quad (10)$$

since $P = Q$ when $t = T$.

Neglecting $e^{\beta T}$,

$$T = \frac{1}{\alpha} \cdot \log \frac{K_1 + K_2 - (V_2 - V_1)}{K_1} \quad . \quad . \quad (11)$$

if a steady state is reached in which the period of flashing is equal to the period of the introduced voltage.

If $L = 0$,

$$\beta = -\infty \quad \text{and} \quad T = CR \log \frac{B - V_1 - v_0 Q'}{B - V_2 - v_0 Q'} \quad . \quad . \quad (12)$$

If $v_0 = 0$, this reduces to the well-known equation for the time of a dark period, first given by Pearson and Anson :

$$T = CR \log \frac{B - V_1}{B - V_2} \quad . \quad . \quad . \quad (13)$$

It will be seen from (12) that the effect of the introduced voltage on the period of flashing will be greater for a given value of $v_0 Q$ the more nearly B approaches V_2 .

Again, if Q is positive, the effect of the introduced voltage is to increase the periodic time; if Q is negative the periodic time is diminished; and if $Q = 0$, the time is unaffected by the introduced voltage.

$Q = 0$ when

$$(1 - LCw^2) \cos \phi + RCw \sin \phi = 0;$$

i. e., when

$$\phi = \tan^{-1} - \frac{(1 - LCw^2)}{RCw}$$

$$[\phi \approx 0 \text{ or } \pi].$$

Q has a maximum value when

$$-(1 - LCw^2) \sin \phi + RCw \cos \phi = 0; \quad \dots (14)$$

i. e., when

$$\phi = \tan^{-1} \frac{RCw}{1 - LCw^2}$$

$$\left[\phi \approx \pm \frac{\pi}{2} \right].$$

Stability of Oscillation.

For stability in a condition of oscillation, after a slight disturbance the system must tend to return to its original condition. For example, if, in the case under discussion, a state of equilibrium has been reached, so that the periodic time of flashing is equal to the periodic time of the introduced voltage, and then ϕ is accidentally increased by some transient disturbance, the resulting effect on the period must be such that the original value of ϕ tends to be restored.

Let us suppose the condition

$$T = \frac{1}{\alpha} \cdot \log \frac{K_1 + K_2 - (V_2 - V_1)}{K_1}$$

to be satisfied, where T = periodic time of introduced voltage, and suppose ϕ lies between 0 and $\frac{\pi}{2}$. This means that the beginning of a dark period occurs *after* the maximum of the introduced voltage.

If a slight increase of ϕ occurs accidentally, the time of the dark period is increased, and the beginning of the next dark period occurs still later; i. e., ϕ is increased. The condition is therefore unstable.

Now suppose ϕ lies between $\frac{\pi}{2}$ and π , and that again the condition

$$T = \frac{1}{\alpha} \log \frac{K_1 + K_2 - (V_2 - V_1)}{K_1}$$

is satisfied.

Here Q is positive, provided that ϕ is

$$< \tan^{-1} \frac{(1 - LCw^2)}{RCw}.$$

But $\frac{dQ}{d\phi}$, and $\therefore \frac{dT'}{d\phi}$ is now negative.

[T' = time of a dark period.]

Hence an increase in ϕ due to a transient disturbance results in a diminution of the time of the dark period, and therefore in a diminution of ϕ . The condition is stable.

Similarly, it may be shown that a stable condition of oscillation is possible if ϕ lies between

$$\tan^{-1} - \frac{(1 - LCw^2)}{RCw} \quad (\text{where } \phi \approx \pi)$$

and

$$\tan^{-1} \frac{CRw}{1 - LCw^2} \quad (\text{where } \phi \approx -\frac{\pi}{2}).$$

Thus the period of flashing may be kept constant and equal to that of the introduced voltage for a certain range of C , R , or B by the automatic adjustment of phase between the introduced voltage and the current in the neon-tube circuit.

The range of control of frequency is determined by the maximum value of $v_0 Q$.

In the foregoing it has been assumed that an alternating voltage of constant amplitude has been introduced into the neon-tube circuit.

It is evident that if the voltage is introduced electromagnetically into the circuit by the motion of the prongs of a tuning-fork maintained by the circuit, v_0 will depend upon ϕ , and, further, the condition that work is done on the fork by the neon-tube circuit must be satisfied.

It is supposed that the mechanical force F acting on the prongs of the fork at any instant is proportional to the current i in the neon-tube circuit at that instant; *i. e.*,

$$F = Ni. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Then the fork will be maintained in its motion if $\int_0^T F \cdot ds$ is a positive quantity, where s is the displacement of the fork from its zero position.

This may be written

$$\int_0^T Ni \cdot \frac{ds}{dt} \cdot dt,$$

remembering that

$$s = a_0 \sin (wt + \phi),$$

where a_0 = amplitude of vibration of the fork.

We have for the condition that the fork will be maintained,

$$\int_0^T i \cdot \cos (wt + \phi) \cdot dt \quad \text{must be positive.} \quad (16)$$

Substituting for i from (4),

$$\begin{aligned} & A_1 \int_0^T e^{\alpha t} \cdot \cos \overline{wt + \phi} \cdot dt + A_2 \int_0^T e^{\beta t} \cos \overline{wt + \phi} \cdot dt \\ & + \frac{(1 - LCw^2)wCRv_0}{(1 - LCw^2)^2 + w^2C^2R^2} \int_0^T \sin \overline{wt + \phi} \cdot \cos \overline{wt + \phi} \cdot dt \\ & + \frac{w^2C^2R^2v_0}{(1 - LCw^2)^2 + w^2CR^2} \cdot \int_0^T \cos^2 \overline{wt + \phi} \cdot dt \\ & \text{must be positive,} \quad (17) \end{aligned}$$

or

$$\begin{aligned} & A_1 \frac{(1 - e^{\alpha T})}{\alpha^2 + w^2} (-\alpha \cos \phi - w \sin \phi) \\ & + A_2 \frac{(1 - e^{\beta T})}{\beta^2 + w^2} (-\beta \cos \phi - w \sin \phi) \\ & - \frac{w^2C^2R^2v_0}{(1 - LCw^2)^2 + w^2C^2R^2 \cdot \frac{T}{2}} \quad \text{must be positive.} \quad (18) \end{aligned}$$

If L is small, the second term may be neglected in comparison with the first.

Thus, since A_1 is positive,

$$-\alpha \cos \phi - w \sin \phi \quad \text{must be positive.}$$

ϕ must therefore lie between

$$\tan^{-1} \frac{CRw}{1 - LCw^2} \quad \left[\phi \approx -\frac{\pi}{2} \right]$$

and

$$\tan^{-1} \frac{\alpha}{w} \quad [\phi \approx \pi].$$

If $L=0$, ϕ lies between

$$\begin{aligned} & \tan^{-1} CRw \\ & \text{and} \quad \tan^{-1} \frac{1}{CRw}. \end{aligned}$$

If it is supposed that the dissipative forces in the motion of the tuning-fork itself are proportional to the velocity, then the work done during one vibration is proportional to

the square of the amplitude of vibration of the fork ; and since the value of v_0 , the maximum voltage induced in the neon-tube circuit, is proportional to the amplitude of vibration, then

$$v_0^2 \propto \int_0^T F \cdot ds ;$$

i. e.,

$$v_0^2 \propto (-\alpha \cos \phi - w \sin \phi) \quad . \quad . \quad (19)$$

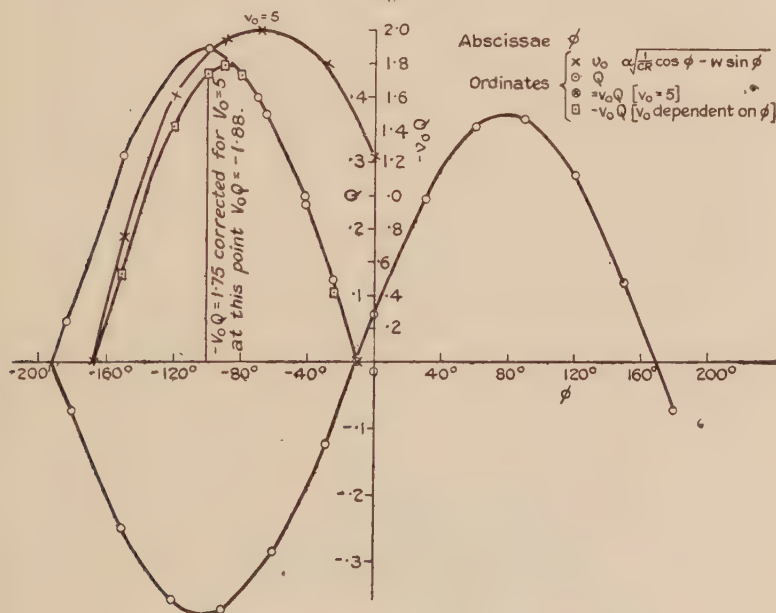
to a first approximation, or

$$v_0 \propto \sqrt{\frac{1}{CR} \cos \phi - w \sin \phi} \quad \text{if } L=0.$$

This gives the relation between v_0 and ϕ^* .

In fig. 2, graphs are given showing the dependence of $v_0 Q$

Fig. 2.



on ϕ , taking approximate values for v_0 (max.), CR , T , and L , to correspond to an experimental case considered in the next Section.

* If the third term of (18) is small compared with the first. v_0^2 is, of course, actually proportional to the sum of the three terms of (18).

In the one case v_0 is considered constant; in the other dependent upon ϕ in the manner shown above.

From equation (18) it is seen that v_0 has its greatest value when $\frac{1}{CR} \cos \phi - w \sin \phi$ has its greatest value; *i. e.*, when $\phi = \tan^{-1} CRw \left(\phi \approx -\frac{\pi}{2} \right)$.

Thus the amplitude of vibration of the fork is (approximately) a maximum when its effect on the period is greatest, and is such that this is shortened by the reaction of the fork on the circuit.

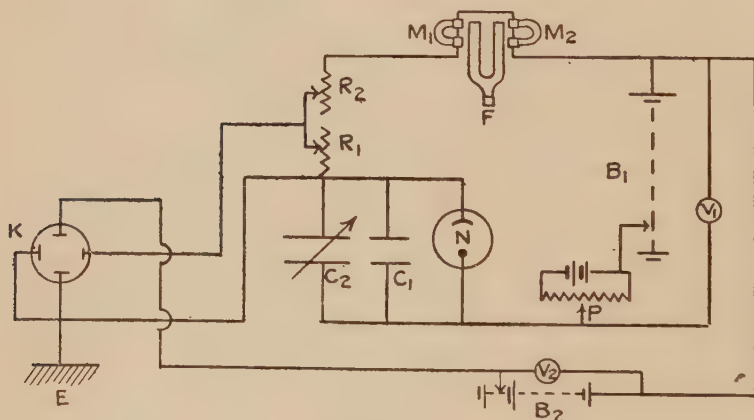
This result is confirmed by experiment.

In the next Section, experiments are described which support the elementary theory outlined in the preceding.

SECTION III.—*Experimental Verification of Theory.*

A fork-controlled neon-tube flashing circuit was set up,

Fig. 3.



- N neon tube.
- C_1, C_2 condensers.
- R_1, R_2 resistances.
- M_1, M_2 telephone magnets.
- F fork.
- B_1, B_2 batteries.
- P potential divider.
- V_1, V_2 voltmeters.
- K cathode-ray oscillograph.

and oscillograph records were obtained of the charging-current and condenser voltage, the apparatus being connected as shown in fig. 3.

The tuning-fork coils were inserted or removed as required by means of a Crawford wireless jack, so that comparisons could readily be made of oscillograph figures with and without the presence of these coils in the circuit.

Records of the oscillograph figures were obtained either by tracing or by means of bromide paper held directly over the fluorescent screen. This latter method was described by Dye in his paper on "An Improved Cathode Ray Tube Method for the Harmonic Comparison of Frequencies" ²¹.

With the tuning-fork coils in circuit, and the tuning-fork free to vibrate, it was found possible to vary one of the constants (battery voltage, resistance, or capacity) of the neon-tube circuit through a considerable range of values, the tuning-fork still being maintained in vibration. As the alteration in value of the electrical constant was made, a corresponding change in the oscillograph figure was seen.

A, B, and C (Pl. III.) are charging current-condenser voltage oscillograph records, obtained with a "Beehive" Osgilby lamp from which the series resistance had been removed.

In A the rate of flashing was increased by the reaction of the vibrating fork on the circuit.

In B the fork had very little effect on the rate of flashing, and was itself not vibrating so strongly.

In C the fork was held so that it could not vibrate.

Records D, E, F (Pl. IV.) are similar oscillograph records obtained with another "Beehive" lamp.

Here D shows the record corresponding to A,

E	„	„	„	B,
F	„	„	„	C,

and G (Pl. IV.) shows the record obtained on removing the tuning-fork coils. (The figure in this case is a straight line corresponding to the equation $B - V - Ri = 0$.)

Record H (Pl. V.) corresponds to A and D, an "I" type lamp (series resistance removed) being used.

Record J (Pl. V.) shows a figure obtained when the frequency of flashing was one-half the frequency of the fork.

In obtaining these and similar oscillograph figures it was noticed that if (say) the battery voltage was adjusted so that the neon-tube circuit was flashing at a suitable frequency, and the fork was released after being held, the oscillograph figure changed with time, the head of the figure charging backwards and forwards like a serpent, and the rate of

change of the figure becoming slower as the fork gained in amplitude, until finally a steady figure was seen. If telephones were included in the neon-tube circuit, the beats could be heard distinctly.

This phenomenon corresponded to the non-uniform beats observed by Appleton⁹ and by the present writer¹⁰, when an alternating voltage of suitable frequency was introduced into a triode-maintained oscillating circuit.

The oscillograph figures show corresponding values of Ri and $(V - V_1)$ in a rectangular coordinate system, where i = charging current and V = condenser voltage.

Since

$$V - V_1 = \frac{1}{C} \int_0^t i \cdot dt,$$

$$C \cdot \frac{dV}{dt} = i.$$

That is, the figures give the relation between $(V - V_1)$ and its differential coefficient with respect to time.

If, therefore, taking the axis of x as the axis of t and the axis of y as $(V - V_1)$, a line is drawn from the origin having a slope $= \left(\frac{i}{C} \right)_{t=0}$, a point may be taken in this line and from it another line drawn, the slope of this being equal to the value of $\frac{i}{C}$ obtained from the oscillograph figure corre-

sponding to the value of $(V - V_1)$ for the point chosen. Proceeding similarly with this second line, and so on, the curve (V, t) is obtained as the envelope of the lines so constructed. The curve (i, t) may be readily constructed from this curve and the oscillograph record.

The shape of the (V, t) , (i, t) curves was obtained this way for one of the earlier figures recorded by tracing. These curves are shown in fig. 4.

To check the results, the apparatus was re-set up as shown in fig. 5, the second neon-tube flashing circuit providing a time-base²⁰ for the charging current of the first. The second neon tube was flashing at frequency 256, the first being controlled by a tuning-fork of frequency 512.

Tracings of the figures seen are shown in fig. 6. It will be seen that they are of the same form as those shown in fig. 4.

Fig. 4.

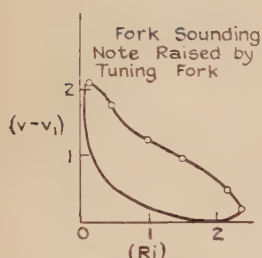


Figure copied from
oscillograph record.

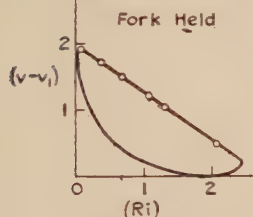


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oscillograph record.

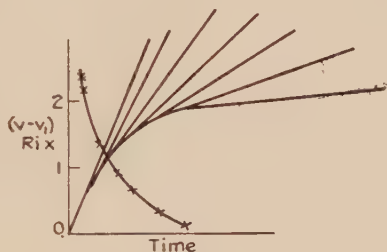
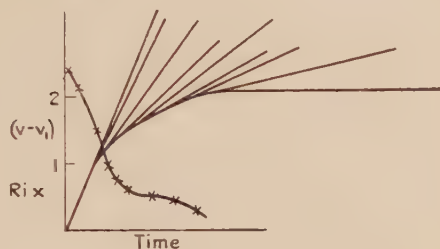
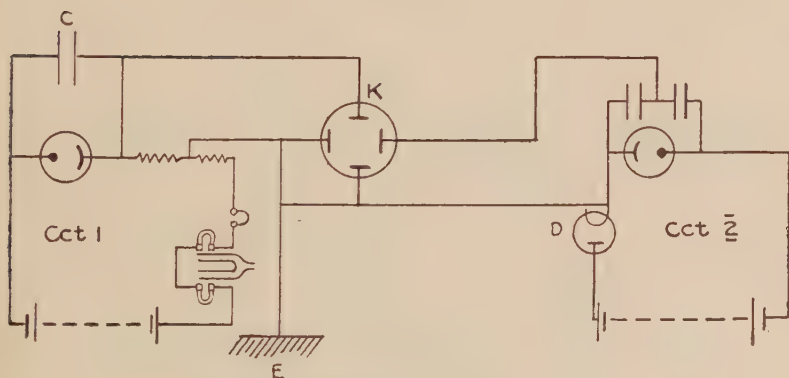


Fig. 5.



K cathode-ray oscillograph.

Cct 2 Neon tube N with condenser C_1 , C_2 in series across it,
these being charged through the diode D (R triode
with grid and filament connected).

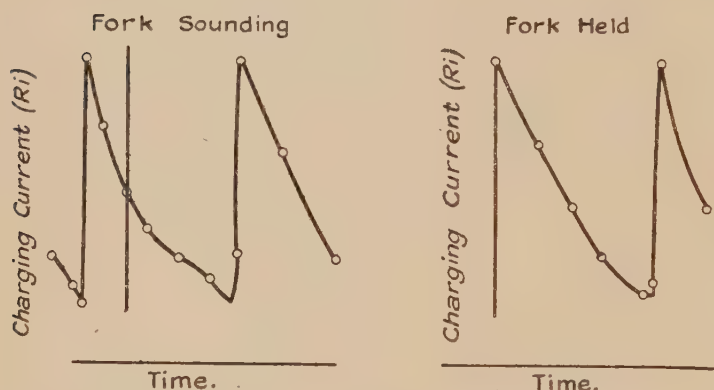
Cct 1 tuning-fork controlled circuit.

Finally, an analysis of the record A was made.

The relation between $(V - V_1)$ and Ri is given by the equation

$$B - V - Ri = v_0 \cos(wt + \phi) + L \frac{di}{dt}. \quad (1)$$

Fig. 6.



The second term on the right-hand side will be of importance only at the beginning of a dark period, since $\frac{di}{dt}$ decreases rapidly with time.

The equation may be written, supposing $L \frac{di}{dt}$ is negligible,

$$V - V_1 + Ri = B - V_1 - v_0 \cos(wt + \phi). \quad (20)$$

When $\cos wt + \phi$ has a maximum or minimum value, the curve approximates to straight lines, given by

$$\text{and } \left. \begin{aligned} V - V_1 + Ri &= B - V_1 - v_0 \\ V - V_1 + Ri &= B - V_1 + v_0 \end{aligned} \right\} \quad (21)$$

The line parallel to these and half-way between them is

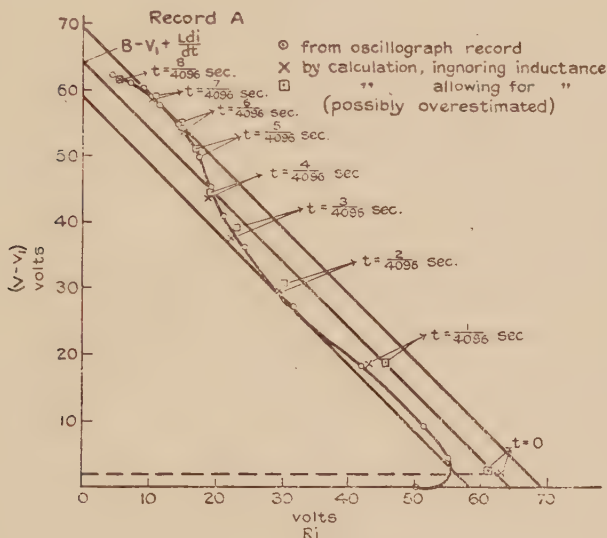
$$V - V_1 + Ri = B - V_1.$$

This cuts the axis of $(V - V_1)$ where $B = V$, a point which cannot, of course, lie on the oscillograph figure, but which gives the value of $(B - V_1)$ if the sensitivity of the oscillograph is known.

The greatest horizontal or vertical distance between the lines represented by equations (21) gives twice the value of v_0 . The value of $(V_2 - V_1)$ is given by the greatest value of $(V - V_1)$ recorded by the oscillograph.

In fig. 7 is shown the graph of $(V - V_1)$ and R_i obtained from record A.

Fig. 7.



The circuit conditions for this record were :—

Total series resistance 88,400 ohms ; oscillograph plates connected across 60,000 ohms.

Parallel capacity $\approx 0.009 \mu F$.

Inductance of tuning-fork coils ≈ 6 henries.

Frequency of tuning-fork 512.

Sensitivity of oscillograph

9.1 volts/cm. for condenser voltage axis.

9.7 " " resistance " "

Using the method outlined above,

$B - V_1$ was found to be 63.75 volts.

$B - V_2$ " " " " 1.75 "

v_0 " " " " 5 "

It was assumed that $\phi = -100^\circ$ (see fig. 2).

Thus $Q = -0.38$, $v_0 Q \max. = -1.9$, which corresponds roughly to the observed possible range of alteration of B without stopping the fork's vibration.

Corresponding values of R_i and $V - V_1$ were obtained, using the values given above and equations (5) and (9).

These values are seen to lie very nearly* on the curve obtained experimentally (except at the beginning), thus showing that the elementary theory given accounts for the phenomena at least to a first approximation. It should be noted that the values of L and C were not known very accurately.

From equation (11), T was calculated.

The actual value of T thus found was too great, but according to the calculations the fork should alter the frequency of flashing by an interval of about a minor third. This was in accordance with observation.

The effect of the presence of inductance in the circuit on the relations between (R_i) and ($V - V_1$) is seen in comparing records E and F.

It will be observed that the critical voltages for the lamp used in obtaining photographs A-C are considerably different from the usual values given for upper and lower critical voltages (160 and 140 volts respectively). The values were about 190 and 127 in this case. For another "Beehive" lamp (used for photographs D-F) the range of alteration of voltage across the lamp was 124-174 volts approximately; for an "I"-type lamp 125-153 volts. In an experiment with the latter there was some indication that the range of alteration of voltage depended on the series resistance†. The variation of the upper and lower critical voltages with circuit conditions has been previously noted by Taylor and Clarkson, Taylor and Stephenson, and Taylor and Sayce²².

Oscillograph figures showing the relation between ($V - V_1$) and R_i have been obtained when the introduced voltage was derived (through a transformer) from a triode-maintained tuning-fork circuit. It was found that, when the rate of flashing was lowered by the introduced voltage, the figure seen differed in shape from any of those seen in the experiments previously described, and corresponded generally to a

* Using the value $B - V_1 = 63.75$ gave points lying consistently above the experimental curve. A rough estimate of $L \frac{di}{dt}$ when $(\omega t + \phi) = \pm 180$ was obtained, and then was subtracted from 63.75 to obtain a corrected value for $B - V_1$. This corrected value was used in the final calculation.

† Larger ranges of alteration of voltage were found in all cases for larger values of the condenser in parallel with the lamp.

value of ϕ lying between $\frac{\pi}{2}$ and π . The figures were complicated, however, by the harmonics present in the introduced voltage.

It has been found possible to control the frequency of flashing by an introduced voltage derived from a second neon-lamp circuit, the frequency of flashing of the second lamp being equal to or a submultiple of that of the first. Oscillograph figures for these experiments have not yet been obtained.

It should be noted that, in the case of the maintained fork, only a small change occurs in the frequency of the fork when one of the constants of the maintaining circuit is varied over the whole of the range of control of frequency.

In a particular experiment it was found that for a fork of frequency 512 a change in frequency of not more than 0.26 per sec. was obtainable.

SECTION 4.—*Conclusion.*

It is clear from the preceding theoretical and experimental discussion that the action of a tuning-fork in holding constant the frequency of flashing of a neon tube may be considered, to a first approximation, as being due to the introduction of a sinusoidal voltage of constant frequency and variable phase into the neon-tube circuit, this voltage being introduced electromagnetically into the circuit by the motion of the prongs of the fork, and the phase of this voltage adjusting itself so that the frequency of flashing is equal to the frequency of vibration of the fork.

In this case of the fork maintained directly by the neon-tube circuit, the range of control is not so great as it would be if a voltage of constant amplitude (equal to the maximum amplitude of voltage introduced by the fork) and frequency were introduced into the circuit: firstly, because less than one-half of the phase-change possible in the second case can occur in the first case; secondly, because the amplitude of vibration of the fork is dependent on its phase with reference to the current in the neon-tube circuit.

The theory is applicable to the case of vibrators maintained electrostatically—*e.g.*, a piezo-electric crystal in parallel with the condenser.

The fundamental equations are then of exactly the same form as equations (1) and (2), the term $L \frac{di}{dt}$ being omitted. The solutions for Ri and T are therefore those given by equations (6) and (12), L being set equal to zero in the latter equation.

The essential characteristics of the electrical vibration in the neon-tube circuit are that the voltage amplitude is constant, and the periodic time dependent on the "time constant" of the circuit and the constant voltage applied to the circuit. The periodic time is practically equal to the time of charging of the condenser.

Any other vibration, electrical or mechanical, of similar characteristics will be affected similarly by a sinusoidal (or other periodic) voltage or force of almost the same frequency introduced either independently or by the reaction of a maintained oscillator (electrical or mechanical).

Thus a similar theory to that given in the preceding pages would explain, to a first approximation, the control of frequency of a multivibrator circuit by an introduced sinusoidal voltage.

The experiments described were carried out in the Physics Laboratory of the London (Royal Free Hospital) School of Medicine for Women.

My thanks are due to the Council of the School for a grant from the Waller Memorial Research Fund for the purchase of a cathode-ray oscillograph.

March 1927.

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XXIX. *The Action of X-rays on Colloids.* By J. A. CROWTHER, M.A., Sc D., F.Inst.P., Professor of Physics in the University of Reading, and J. A. V. FAIRBROTHER, B.Sc.*

Introduction.

THE investigations described in the present paper were undertaken primarily in the hope of obtaining some light on the mechanism of the action of X-rays on living matter. It was hoped that if the nature of this action could be elucidated for some of the simpler inorganic colloids a basis might be found from which to attack the more complex problem presented by the organic colloids which make up such a large proportion of the living cell. The colloidal state is also interesting in itself, and further information as to the electrical condition of the colloid particle might possibly emerge from a detailed study of the action of the rays upon it.

In order to avoid as far as possible complications which might arise from the chemical action of the radiation either on the colloid particles themselves or on the solvent, it was decided to employ in the first place hydrosols of the elements, principally metallic. Preliminary experiments showed that these sols were relatively insensitive to the action of X-rays, and that very large quantities of radiation were required to produce any sensible change in them; and further that, when exposed in shallow dishes for the long periods required for irradiation, the sols were liable to be affected seriously by factors not directly connected with the radiation, of which impurities in the atmosphere were probably the most important.

Experimental Details.

The source of radiation in all the experiments was a Shearer tube fitted with a molybdenum anticathode, taking a current of 4 m.a. at a P.D. of 55,000 volts, supplied by a large induction coil and a mercury break. The rays emerged through a thin aluminium window, and subsequently passed through a cover-slip of glass 0.15 mm. thick. The mean value of the mass coefficient of absorption in aluminium of the resulting radiation was 4.6. This corresponds to the absorption coefficient of molybdenum K-radiation. The

* Communicated by the Authors.

radiation is no doubt heterogeneous, but a considerable proportion of it must consist of the molybdenum K-radiation.

The colloid to be exposed was contained in a shallow dish, usually of fused quartz, which when filled to a depth of 0.8 cm. held about 2 c.c. of the solution. A covering vessel, the top of which was closed by a glass cover-slip 0.15 mm. thick, was placed over the dish containing the solution, and sealed down with molten paraffin wax. The colloid was thus hermetically sealed throughout the exposure. An equal volume of the same solution was placed in a similar dish and sealed in the same way. This served as a control for the experiment. The colloid after exposure was always compared with the control, and not with the stock solution. It was hoped that any effect which might be due to the mere exposure of the colloid in a shallow vessel would thus be eliminated. The results obtained in this way were found to be consistent.

The radiation was measured by an air-gap ionization chamber, connected to a gold-leaf electrometer, and a standard microfarad condenser. The quantity of radiation required to charge the condenser to a P.D. of 1 volt was taken as a convenient unit for the experiments. Since the volume of air between the electrodes in the ionization chamber was 1 c.c., this represents a dose of 3000 e. units received by the ionization chamber, the aperture of which was placed at 10 cm. from the anticathode of the tube. The surface of the colloidal solution was usually at a distance of 2.0 cm. from the focal spot, so that the dose received by the colloid was 25 times greater, or 75,000 e. The quantity of radiation necessary to produce erythema on the skin is usually reckoned at about 1000 e. The quantity of radiation corresponding to our experimental unit, which will be referred to as 1 mc., is very considerable. The time taken to give a dose of 1 mc. was about 8 minutes.

General Results.

Iron (Bredig solution). Exposures up to 14 mc. produced no apparent change in the appearance of the solution, and no signs of precipitation. The exposed and control solutions were each treated with two drops of very dilute potassium chloride solution. The sol which had been exposed coagulated completely, leaving a colourless liquid. The control showed no coagulation. An additional 6 drops of the same potassium chloride solution were required to produce any visible coagulation in the control. The iron has thus been rendered less stable by the radiation.

Copper (Bredig solution). Coagulation begins when the exposure reaches 11 mc., the amount precipitated increasing with increasing exposure. A dose of 14 mc. precipitates exactly one-half of the colloidal copper from solution. The case of copper is considered in more detail in a later section of the paper.

Silver (Bredig). As prepared by arcing under water this is a dark greenish-black solution. Under prolonged exposure to the radiation, the solution became clearer, and turned distinctly reddish in colour. The change in colour indicates increasing dispersion in the colloid, and increased stability.

Silver. (Collosol Argentum, kindly supplied by the Crookes Laboratories.) This is a protected colloid, and the solution is orange in colour. After exposure to X-rays the colour changed to a dark red. This would indicate increased dispersion. The exposed sol and the control were examined under the ultramicroscope. The control showed a certain amount of aggregation into clusters; the exposed sol contained only single particles. Counts of the relative numbers of particles in the two sols were made by means of a micrometer eyepiece. The average number of particles per square in the eyepiece was 1.16 in the exposed sol, and 0.61 in the control. The exposure was 25 mc.

Gold. (Collosol Aurum, unprotected.) This was a sample of colloidal gold as prepared for Lange's test. Its colour was pink with a distinctly violet tinge. Prolonged exposure to X-rays changed the colour to a clear red. When equal numbers of drops of very dilute electrolytes were added to the two samples, the control precipitated while the exposed remained in solution.

In further experiments a small number of drops of copper sol were added to the gold sol before exposure. After a dose of 5 mc. both the exposed and the control sols were perfectly clear. On warming to boiling-point in quartz test-tubes, the unexposed sol precipitated, while the sol which had been irradiated remained clear.

We may sum up this section by saying that in the case of iron and copper sols the X-rays produce coagulation; in the case of silver and gold the irradiation produces a greater degree of stability in the sol. It may be noted that iron and copper sols are kationic, while gold and silver are anionic.

*A Further Investigation of the Action of X-rays on
Copper Sols.*

Of the colloids investigated, the Bredig copper sol seemed the most suitable for a more detailed study. It is easily prepared in large quantities by arcing under distilled water, and the sol so obtained can be preserved for some months in quartz flasks without any precipitation occurring. The amount of copper in solution at any time can rapidly be determined by titrating with a very dilute solution of nitric acid of known strength, a method due to Paine. Nitric acid dissolves the copper sol without coagulation, and the change in colour from the dark red of the sol to the practically colourless copper nitrate solution is very marked, and gives an excellent end-point for the titration. In this way it was possible to make estimations to an accuracy of about 5 per cent., even with the very small volumes of sol which could be exposed at one time to the radiation (about 2 c.c.).

After exposure to X-rays the sol was transferred to a quartz test-tube and boiled for two minutes. It was then allowed to stand for half an hour and subsequently centrifuged for two minutes, so that any precipitate which might have formed was thrown to the bottom of the test-tube. By means of a pipette 1 c.c. of the clear liquid was withdrawn from the test-tube, and immediately titrated. The sol used as a control was treated in exactly the same manner. The ratio of the volume of acid required to dissolve the copper remaining in suspension in the exposed sol to that required for the control was taken as a measure of the proportion of copper which had not been precipitated by the radiation. Numerous tests showed that consistent results could be obtained by this procedure.

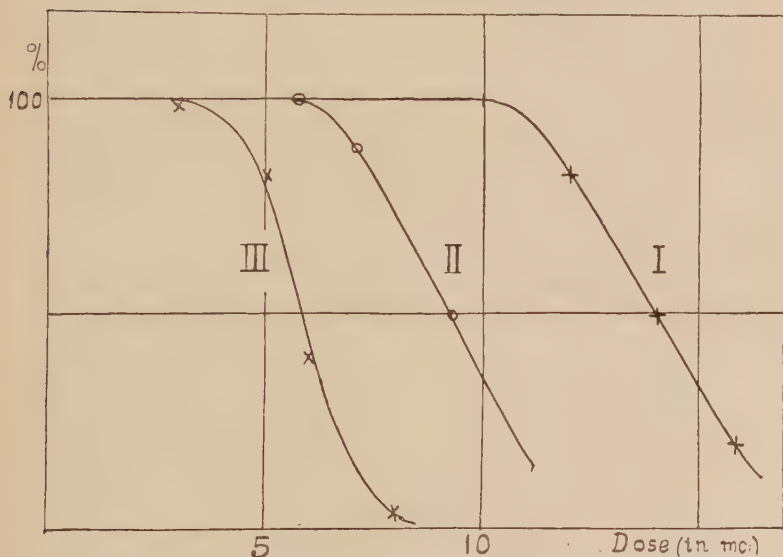
As sols prepared at different times might be expected to vary somewhat in concentration, and size of particles, sufficient sol was prepared for a series of experiments. The copper sol changes in colour for some days after preparation, indicating some change either in the composition or in the size of the particles. The sol was allowed to stand for a week or more before use. The mobility of the sol was then measured by the U-tube method, and was found to be 2.5×10^{-4} cm. per sec. per volt per cm., giving a value for the electrokinetic potential of 0.035 volt. Attempts were also made to determine the size of the particles from the rate of settling of the sol under gravity, using the alternating field method described by Burton*. The experiments were not very satisfactory, as the surface

* Burton and Reid, Phil. Mag. vol. 1. p. 1221 (1925).

always became very diffuse before the end of the experiment. The velocity of settling was found to be approximately 4.7×10^{-6} cm. per sec., measuring always the upper boundary of the diffuse layer. This gives the radius of particles as 5.2×10^{-6} cm. This value is probably a minimum. Using the same method for a similar Bredig copper sol, Burton found a value for the radius of the particles of 7.1×10^{-6} cm.

Percentage of Copper remaining in solution after various doses of X-rays.

- I' Pure sol.
- II Sol containing 2.4×10^{-6} gm. ferricyanide per c.c.
- III Sol containing 3.9×10^{-6} gm. ferricyanide per c.c.



The copper sol was then exposed, in a series of experiments, to varying doses of X-rays. The results of these exposures are recorded in the curve I of the figure. Coagulation begins when the dose exceeds 10 mc. and the sol is half coagulated with a dose of 14 mc. It is evident that some of the particles require considerably larger quantities of radiation to produce precipitation than others. This is possibly due to a variation in size of the particles. It is possible, however, that it is due to the fact that, owing to absorption in the upper layers, the radiation reaching the lower levels in the sol is distinctly reduced in intensity. It

was impossible to stir the sol during exposure, and the diffusion and chance convection currents may not have been sufficient to maintain a thorough mixing of the solution during the exposure.

A series of experiments were then made in which the sol was "sensitized" before exposure by the addition of minute quantities of some coagulating substance. For this purpose we employed a very dilute solution of potassium ferricyanide. It was found that, with the method of experimentation we adopted, the addition of 7.2×10^{-6} gm. of this salt to 1 c.c. of the copper sol caused the precipitation of half the copper. To two portions of the original copper sol we added quantities of the ferricyanide solution, so as to make the concentration of ferricyanide in the one up to 2.4×10^{-6} gm. per c.c., and in the second up to 3.9 gm. per c.c. These solutions were then given a series of doses of radiation, and the amount of copper remaining in solution was determined as before. The results are shown in curves II and III of the figure, curve II referring to the sol with the smaller proportion of ferricyanide. It will be seen that the amount of radiation required for coagulation becomes smaller as the concentration of ferricyanide increases.

The results, in fact, indicate a numerical equivalence between the radiation and the electrolyte in their coagulating powers. Thus 7.2×10^{-6} gm. of salt in 1 c.c. of sol produce the same coagulation as a dose of 14 mc.; 3.9×10^{-6} gm. reduce the dose of radiation required by 8 mc., and 2.4×10^{-6} gm. reduce the dose by 4.5 mc. The ratio of the quantity of radiation to the amount of salt which produces the same effect is thus 1.95, 2.05, and 1.88 respectively. A concentration of potassium ferricyanide in the sol of 10^{-6} gm. per c.c. is equivalent in its coagulating action to a quantity of radiation measured by 2 mc. in the ionization chamber, *i. e.* to 150,000 e. received by the sol.

Precisely similar results were obtained when the copper sol was sensitized by the addition of small quantities of a negative colloid, such as the unprotected gold sol previously described. It was found that 10^{-5} gm. of gold per c.c. of copper sol was equivalent to 100,000 e. of radiation.

In these experiments the sensitizing agent was added before the exposure, as this is the most convenient way of carrying out the experiment. The effect, however, does not depend on the presence of the sensitizer during the process of irradiation. Practically the same results are obtained if the sol is irradiated first, and the sensitizer is added after the completion of the exposure. Thus if the

pure sol is given 6 mc. of radiation, which leaves it quite clear, and subsequently is mixed with an amount of potassium ferricyanide solution which would, together with the X-rays, have caused the coagulation of half the sol if it had been present at the time of radiation (3.9×10^{-6} per c.c.), 40 per cent. of the copper coagulates. The amount precipitated is thus, within the limits of experimental error, the same as if the salt had been present throughout. Thus the effects of the radiation and the sensitizer, while additive, seem to be completely independent.

Discussion of Results.

The experiments described provide only a preliminary survey of a wide field in which few observations appear to have been made. Fernau* has reported that cerous hydroxide and albumin are coagulated by X-rays, and Wels and Thiele† have found that globulin sols are aggregated by irradiation, a result which so far we have been unable to confirm. In a nearly related subject, Hardy‡ has shown that positively charged globulin sols are coagulated by β -radiation from radium, while negatively charged sols are rendered more disperse. Fernau also records the coagulation of cerous hydroxide by β -radiation.

As a preliminary step to a discussion of the subject, it may be well to record some approximate data on the physical action of X-radiation. A dose of 1 e., by definition, allows the transference of 1 electrostatic unit of electricity across 1 c.c. of air. The number of pairs of ions formed per c.c. in air by the passage of 1 e. is thus $1/4.774 \times 10^{-10}$ or 2.1×10^9 . The number of pairs of ions per gm. of air is thus 1.7×10^{12} . This will also be approximately the number of pairs of ions formed per gm. in water, since for elements of low atomic weight ionization is largely a mass effect. In our experiments, however, the depth of solution employed was sufficient to produce a considerable absorption of the radiation, so that the lower layers received a smaller dose of radiation than the upper. A correction can easily be applied if the coefficient of absorption of the rays is known. For the depths used in our experiments the correcting factor is 0.7. Thus the average number of ions per gm. of sol for a dose of 1 e. received by the surface is 1.2×10^{12} , or 9×10^{16} for our experimental unit dose.

Ionization is, however, a secondary effect produced by the

* Fernau, *Kolloid-Zeit.* xxxiii. p. 89.

† Wels and Thiele, *Arch. ges. Physiol.* ccix. p. 49.

‡ W. Hardy, *Proc. Camb. Phil. Soc.* p. 201 (1903).

action of the photoelectrons ejected by the X-rays. If we assume that the radiation is mainly molybdenum K-radiation, each of these photoelectrons is responsible for about 600 pairs of ions. The number of photoelectrons ejected per gm. of water is thus 1.5×10^{14} for a dose of 1 mc. as recorded by our electroscope. Since the mass absorption coefficient of X-radiation in copper is 45 times that in water, the number of photoelectrons ejected per gm. of copper is 6.7×10^{15} . Taking the radius of the copper particles in the sol as 5.2×10^{-16} cm., the average number of photoelectrons ejected from a particle during a dose of 1 mc. is about 35. Thus during the irradiation necessary to produce coagulation in the copper sol each particle will eject about 500 photoelectrons, and will thus gain a *positive* charge of 500 e , where e is the electronic charge.

If the stability of the colloid depends on its electrical charge, as is usually assumed, the positive colloids should become more stable, the negative colloids less stable, from the loss of these electrons. This is exactly the reverse of what is indicated by our experiments. The particles will, it is true, receive a certain number of photoelectrons from the surrounding medium, but it is improbable that the number so gained will be more than a small fraction, say 10 per cent., of those which it ejects. The loss of photoelectrons then, so far from being the direct cause of coagulation, appears as an effect which the true coagulating agent must overcome.

The total number of ions produced in 1 c.c. of sol during the exposure required to coagulate the copper sol is $14 \times 9 \times 10^{16}$, or 1.26×10^{18} . The same effect is produced by 7.2×10^{-6} gm. of potassium ferricyanide, which contain 1.2×10^{16} trivalent ferricyanide ions. The total ionization produced by the radiation is thus amply sufficient to neutralize the charges on the colloid particles. That the amount of X-ray ionization required should greatly exceed the electrolytic ionization is only to be expected, since the rate of recombination for the X-ray ions is likely to be large. Only those ions which come within the electrical field of the colloid particles would be likely to be effective, the remainder simply recombining *in situ*.

This conception of the action of the radiation can easily be treated numerically. If we assume that the electrokinetic potential ζ is due to a charge q on a particle of radius r , and that an electrical double layer surrounds the particle of mean thickness δ , and dielectric constant = D , then

$$q = \frac{Dr(r+\delta)\zeta}{\delta} = \frac{Dr^2\zeta}{\delta} \text{ (approx.)}.$$

If n is the number of ions formed in unit volume of the solution by the amount of radiation required to produce coagulation, and if we assume that all these ions cross the double layer without recombination, the total charge conveyed across the double layer during the exposure will be $ne \times (\text{volume of double layer}) = ne4\pi r^2\delta$ approximately. Thus, assuming that coagulation will take place when the charge q has been neutralized,

$$Dr^2\xi/\delta = 4\pi ner^2\delta; \quad \delta^2 = D\xi/4\pi ne.$$

The ionization at the surface of a copper particle will, however, be greater than that in the bulk of the solution, owing to the greater emission of photoelectrons from the copper. For particles as small as those in colloidal solution the effect will increase with the size of the particle. Taking the radius as 5.2×10^{-6} cm., it can be shown that the ionization at the surface of the particles will be approximately 4 times that in the bulk of the solution. Since the ionization increases with the size of the particle, the coagulating effect of the radiation is not really independent of the radius of the particle, although the radius does not occur explicitly in the formula.

For the copper sol employed in our experiments we have $n = 4 \times 1.26 \times 10^{18}$, $\xi = 0.035$ volt or 1.17×10^{-4} e.s.u., $D = 81$, and $e = 4.774 \times 10^{-10}$ e.s.u. Thus δ , the thickness of the double layer from which the ions are drawn, works out at 5.6×10^{-7} cm., and q , the initial charge on the colloid particle, at 4.4×10^{-7} e.s.u. A more exact calculation, allowing for the charges carried away by the photoelectrons, gives $\delta = 7.2 \times 10^{-7}$ cm.

The value of δ thus obtained is of the order of magnitude generally accepted for the equivalent thickness of the diffuse double layer surrounding a colloid particle. Hevesey*, for example, assumes a value 5×10^{-7} cm. The average electric field in this layer must be of the order of 7×10^4 volts per cm., and it is not unreasonable to suppose that with a field of this order any ions formed in the diffuse double layer would be carried across it without appreciable recombination, even in a liquid medium. There seems, thus, to be some support for the hypothesis that the discharge of the copper colloid is due to the ions formed by the radiation in the diffuse double layer.

The difficulty in accepting this interpretation of the phenomena lies in the fact that, so far, we have not succeeded in

* v. Hevesey, *Kolloid. Zeits.* xxi. p. 129 (1914).

producing coagulation in any negative colloid. We should expect that the presence of free ions would neutralize any electrical double layer, no matter what its sign, whereas the evidence, as far as it goes, indicates that the negatively charged colloids, silver and gold, are rendered somewhat more stable by irradiation. The difficulty is, perhaps, not insuperable. It has been suggested that the metallic particles which form the nucleus of the colloidal micelle are, in the case of the noble metals, actually positively charged, the negative electrokinetic potential being due to an excess of negative charges on the surface of the micelle, where the slipping actually takes place when the particle moves. The ejection of photoelectrons would make the positive nucleus more positive, and thus enable it to hold a larger negative charge. For the copper particles the charge gained by the ejection of negative electrons is smaller than the charge lost by ionization in the diffuse double layer, but the two are of the same order. Since the coefficient of absorption of X-rays is twice as great for gold as for copper, gold will lose electrons at a greater rate than copper, and it is thus quite conceivable that for the gold particles the direct gain of positive charge due to this cause may more than counterbalance the loss of charge due to the ionization currents. Further experiments are in progress to test this suggestion further.

There remains, of course, the further possibility that the action of the radiation may be indirect: that is to say, the X-rays may produce in the sol some chemical substance which in turn acts on the colloidal particles to produce precipitation. Hydrogen peroxide is an obvious suggestion in this connexion. Clark * has, in fact, already put forward the suggestion, in connexion with Fernau's observations on the precipitation of cerous hydroxide, that coagulation is due to the formation and subsequent decomposition of hydrogen peroxide in the solution. Freundlich †, however, states definitely that the addition of hydrogen peroxide to a cerous hydroxide sol has no effect on its stability, so that Clark's suggestion seems to be untenable in this case. Bredig sols of copper and iron are coagulated by quite small quantities of hydrogen peroxide. In order to test the matter further we irradiated a quantity of distilled water under the same conditions as those employed in irradiating the sols. We were unable to detect any trace of hydrogen peroxide in the irradiated water, although the test employed

* Clark, 'Applied X-rays,' p. 78.

† Freundlich, 'Colloid and Capillary Chemistry,' p. 486.

(chromic acid test) would certainly have revealed the presence of as little as one-tenth of the concentration necessary to produce coagulation. It seems improbable, therefore, that hydrogen peroxide plays any appreciable part in the phenomena.

Summary.

It is shown that certain colloidal solutions are affected by exposure to large quantities of X-radiation. Positively charged colloids are coagulated by irradiation, but negatively charged colloids have their stability increased. The effect is studied numerically for a Bredig Copper sol. It is suggested that the coagulation is brought about by the ionization produced in the diffuse double layer surrounding the particles.

The expenses of this research were partly met by a grant from the Government Grants Committee of the Royal Society, to whom we express our best thanks. We are also much indebted to Mr. Ward, and the Crookes Laboratories, for their kindness in supplying us with a number of colloidal solutions.

Department of Physics,
The University of Reading.
May 19, 1927.

XXX. *On the Absolute Zero of Entropy and
Internal Energy.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I READ with much interest the paper of Prof. R. D. Kleeman "On the Absolute Zero of Entropy and Internal Energy" in the *Phil. Mag.* of April 1927. Will you allow me to make some remarks?

1. I do not agree with the author about his conclusion that the conditions $\left(\frac{\partial U}{\partial T}\right)_v = 0$ and $\left(\frac{\partial S}{\partial T}\right)_v = 0$ at $T=0$ are necessary mathematical consequences of the fact that U and S are minimum for $v = \text{const.}$ at the absolute zero of temperature. We know several examples of physical quantities which reach

a minimum value without satisfying the conditions of an analytical minimum, because the variable has no physical meaning beyond the limit for which the quantity reaches the minimum value. So the density δ of a mixture may be a minimum for the concentration $c=0$, because a negative concentration is a physical impossibility, but mathematically

δ has a value for a negative c and $\frac{d\delta}{dc}$ is not necessarily zero.

The same may be—or rather is—the case for the energy and entropy as functions of the absolute temperature; $T=0$ is only a physical limit, and so the values of U and S may be minimum at $T=0$ only because negative temperatures do not exist. Let us take for example the thermal energy of a classical ideal gas: *per definitionem* it is proportional to the

absolute temperature; at $T=0$ it is zero, but $\frac{dU}{dT}$ is not zero, just owing to the choice of the temperature scale. Why

then should $\left(\frac{\partial U}{\partial T}\right)_v$ be necessarily zero at $T=0$ for a condensed state?

The fact that $c_v = \left(\frac{\partial U}{\partial T}\right)_v = 0$ for the solid state at $T=0$ has not merely a mathematical reason, but is a physical fact which must be accounted for by theoretical considerations (quanta).

For the same reason $\left(\frac{\partial S}{\partial T}\right)_v$ is not necessarily 0 at $T=0$, but when $\left(\frac{\partial S}{\partial T}\right)_v = 0$, then $\left(\frac{\partial U}{\partial T}\right)_v = 0$, for

$$T \left(\frac{\partial S}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v \quad \dots \quad (a)$$

2. Nor do I agree with the conclusion $c_{v\infty} = 0$ at $T=0$, for even when $T=0$ the integral term of equation (10) may have a finite value, the integration extending over an infinite increase of the volume.

3. It seems to me that the fact that $\left(\frac{\partial U}{\partial T}\right)_v$ and $\left(\frac{\partial p}{\partial T}\right)_v$ are always positive may not be accounted for by general considerations, and I am not quite sure that one could not imagine systems in which those conditions would not be verified. I think we must consider those conditions as physical facts which we may try to explain by mechanical representations.

Certainly the fact that $\left(\frac{\partial U}{\partial T}\right)_v$ is positive is connected to that other, that adiabatic expansion is attended by a decrease of temperature, but even this is not necessary, and I should say it is a consequence of the first. In other words $\left(\frac{\partial v}{\partial T}\right)_s$ is negative because

$$\left(\frac{\partial U}{\partial T}\right)_v + T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_s = 0,$$

and $\left(\frac{\partial U}{\partial T}\right)_v$ and $\left(\frac{\partial p}{\partial T}\right)_v$ have positive values.

4. According to equation (a), $\left(\frac{\partial U}{\partial T}\right)_v$ and $\left(\frac{\partial S}{\partial T}\right)_v$ are both positive. Consequently U and S are both minimum (for $v = \text{const.}$) at $T=0$. Besides, according to $\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$ S increases with v even at $T=0$, and so the absolute minimum of entropy (zero of entropy), at which again $\left(\frac{\partial S}{\partial v}\right)_T$ is not necessarily zero, should not correspond to the solid state under pressure 0 at $T=0$, unless this solid state be incompressible, which is to be admitted, as it seems.

As for U, according to $\left(\frac{\partial U}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p$, $\left(\frac{\partial U}{\partial v}\right)_T = -p$ at $T=0$ for the solid state, so that U increases as well by compression as by traction (negative p). By vaporization, even at $T=0$, U increases also and so U is indeed minimum for the solid state under pressure 0. For that state $\left(\frac{\partial U}{\partial v}\right)_T$ is really zero.

But if the solid state at $T=0$ is compressible, the line *ab* of minimum entropy (see fig. at page 890) ought not to pass through point U_0 : it should pass under that point; and the zeros of entropy and energy would not coincide.

Yours sincerely,

Prof. Dr. J. E. VERSCHAFFELT,

70 St.-Pietersnieuwstraat,
Ghent, April 7, 1927.

Professor of Physics at the
University of Ghent.

XXXI. *Dr. Jeffreys and the Earth's Thermal History.**By J. JOLY, F.R.S.**

IN a recent number of the 'Geological Magazine' Dr. Jeffreys deals with the subject of the earth's thermal history (Geol. Mag. Nov. 1926, p. 520). In the course of his remarks he refers to a theory of the earth's surface history for which I am responsible†, and repeats certain arguments directed against the fundamental proposition that the alternate accumulation and discharge of heat of radioactive origin was accountable for the cyclical nature of earth-history. He now expresses his arguments as follows :—

"Whenever a physical system of finite extent free to lose heat by radiation from an outer boundary is affected by a steady internal source of heat, the temperature at any point will approach steadily towards some permanent value as a limit, and there will be no possibility of a permanent oscillation of temperature. So long as the system is solid this proposition can be proved easily ; fusion, if it occurs, complicates the mathematics, but leaves the result no less evident physically. Joly complicates the issue further by assuming that the outer crust revolves under tidal forces ; this introduces the possibility of some oscillation of temperature, but not enough to produce resolidification, and is open to objections on its own account."

In this statement, which Dr. Jeffreys designates his "main conclusion," he is tacitly assuming that no relative motion of the parts of the medium takes place. That this is so will be shown later by several instances of cyclic phenomena arising out of steady supply of heat.

In his earlier paper he writes as follows :—"The basic rocks below the granitic layer also contain radioactive matter, and it is upon the heat generated in them that Prof. Joly relies for his main object, which is to explain periodic variations in temperature within the crust." (Phil. Mag. May 1926, p. 924.)

My comment on this earlier statement was to the effect that it does not describe the conditions I have all along discussed. My "main object" has been to show that there is a periodic accumulation and discharge of heat. But the heat is latent, and there is but little variation of temperature. That Dr. Jeffreys has not entered into the significance of

* Communicated by the Author.

† 'The Surface History of the Earth' (Oxford, 1925).

these conditions is shown by his assumption that the only way periodicity can arise is by a trigonometrical time-factor in the expression for conduction.

A clear statement of what is fundamentally involved in my theory of surface history will render the issues more readily understood. Mr. J. R. Cotter, in his paper "On the Escape of Heat from the Earth's Crust" (*Phil. Mag.* Sept. 1924, p. 458), gives a lucid and concise summary of the thermal conditions as follows:—

"According to Prof. Joly's theory, that portion of the earth's crust immediately beneath the ocean-floor consists of basalt, in which a continual generation of heat takes place, owing to the presence of radioactive materials. Prof. Joly concludes on experimental grounds that the heavier ultra-basic materials which probably underlie this stratum of basalt are much less radioactive. For the purpose of simplifying the investigation, I shall assume that no transmission of heat occurs through that horizon which may be regarded as the lower boundary of the basalt. The modifications which would have to be made in the theory when radioactivity of the underlying rock is taken into account need not here be considered. The temperature of the upper surface of the basalt will be taken to be 0°C. , which is approximately the temperature of the ocean-floor.

"Let us suppose that at some stage in the history of the earth's crust the basalt is solid throughout. As we descend from the upper surface the temperature will rise until at a certain depth the melting-point of basalt is reached. If we denote the melting-point by θ_0 then we can call this horizon the θ_0 geotherm. Below this level the rock is supposed to be everywhere at its melting-point. The temperature will not be quite uniform, but will increase slowly with depth, since the melting-point of basalt rises with increase of pressure. A long period of quiescence will ensue, during which the radioactive heat generated above the θ_0 geotherm will escape by conduction through the ocean-floor, while below this geotherm the heat generated will become latent owing to liquefaction of the rock, the temperature remaining steady all the time. It seems probable that the material in this lower portion would preserve its rigidity till an advanced stage of liquefaction has been reached, being in a condition somewhat like that of a sponge filled with water. A period of activity would now set in, starting with the breakdown of the weakened material owing to the disruptive action of tidal forces. Circulation might begin slowly, but would rapidly increase, because the descending portions would tend

to solidify owing to increase of pressure, so that the increase of density due to solidification would accelerate the rate of descent; while the ascending portions would become more fully liquefied and would rise faster. As soon as circulation became general, a precipitate of solid material would begin to be formed at the bottom of the liquid mass; while at the same time the rest of the medium up to the θ_0 geotherm would become quite fluid, its temperature being nearly uniform and equal to the temperature of the solid deposit—that is, the temperature of the melting-point of basalt at a pressure equal to that of the fluid at its lowest level. Thus the upper part of the fluid would be above the melting-point appropriate to its pressure, and it would begin to melt away and to erode the solid rock above it—that is, it would push the θ_0 geotherm upward. This process would be comparatively rapid at first, but would fall off owing to two causes: first, because as the fluid became shallower owing to the deposit of solid, its temperature would fall, and secondly, because the loss of heat by conduction through the ocean-floor would become accelerated as the geotherms rose. Prof. Joly thinks that the θ_0 geotherm would rise to within a very few miles of the surface. It would, however, finally become stationary, and then descend. At this stage the escape of heat would be very rapid, and the rate of solidification at the bottom would also be rapid. There seems little reason to doubt that the whole would eventually become solid again, and cooling would go on till it recovered its initial condition and initial distribution of temperature. The whole series of changes would form a cycle which would be repeated.”

It will be seen that the changes of temperature involved are mainly confined to those arising out of the movement of the θ_0 geotherm and to those due to the change of melting-point with depth. It will also be noticed that only intermittently can the substratum lose heat “from an outer boundary,” *i.e.* attending the upward movement of the θ_0 geotherm. It is just this fact which leads to accumulation of heat and gravitational instability in the depths. Since we must infer from Dr. Jeffreys’s references to this matter that he does not accept the general statement as to the importance of latency, and is basing his conclusions upon abstract considerations which do not take account of the conditions actually involved, I think it desirable to deal with the subject more definitely and practically. The main object of the present paper is, then, to show that conditions of cyclic change of state arising out of steady

thermal flux are not only open to our inspection in nature, but are reproducible in various forms in the laboratory. I shall first refer to the well-known and well-investigated phenomena of the geyser.

The conditions responsible for the periodic phenomena of the geyser, as investigated in the first instance by Bunsen and subsequently by others, may be described as follows:—

Heat of volcanic origin, entering steadily from the walls of a deep well, raises the temperature of the water till the boiling-point proper to the depth is nearly attained at all levels. If, then, the boiling-point is finally reached at any particular level, change of state at that level occurs; then follows expulsion of water at the top, reduction of pressure at all levels, and general breakdown of equilibrium. The sudden production of water vapour occasions the explosive ejection of both water and steam in a succession of paroxysmic jets. The water falling back into the well is now everywhere super-cooled respecting the local boiling-point. The steady accession of heat, which continues throughout, once more raises the temperature at all levels till conditions of instability again arise, when the phenomena are repeated.

It will be recalled that Tyndall realized these conditions experimentally and with perfect success ('Heat a Mode of Motion,' p. 124 *et seq.*). He used a vertical tube filled with water, applying a steady source of heat at the lower end. The local change of state at a higher level, which precipitates instability, was represented by a steady additional supply at a higher level. But it is sufficient to supply a steady source of heat to the lower part of the tube.

An interesting paper on the subject of geysers by T. A. Jager appears in the 'American Journal of Science' (1898, vol. i.). He writes (p. 324): "The accuracy of Bunsen's theory was early confirmed by experiment, and the only mechanism necessary to produce geyser eruptions is a tube filled with water, open above and heated below." He states with reference to the well-known geyser "Old Faithful" of the Yellowstone:—"It takes practically a uniform period, some 65 minutes, to heat the new column to a state of ebullition at its base, and has done so for 28 years of human record; it is fair to assume that the heat-supply is constant." From this it follows that over 240,000 of these "revolutions" had taken place within human record up to the year 1898.

When water flows away at the top of a geyser some must enter from beneath to supply its place, but, as both theory and experiment show, this condition is not essential to the

periodic activity of the geyser. If a geyser basin exists and the cooled water is returned to the tube, the steady heat-supply beneath is sufficient to maintain the "oscillation of temperature" which from Dr. Jeffreys's statement would seem to be impossible.

Let us now imagine that we are dealing with a medium such as constitutes the substratum. It is, we will suppose, in a state of quasi-rigidity. It receives throughout a steady thermal supply. This thermal supply is not the same at all levels. It is, by a curious law affecting a heterogeneous medium of this sort in a gravitational field (*Phil. Mag.* June 1927, p. 1233 *et seq.*), richer in radioactive elements in its higher than in its lower levels. The physical state of the medium is not the same at all levels. In the depths the temperature required for liquefaction is higher than in the upper parts. But the precise distribution of thermal energy cannot be defined. It will depend upon the previous history of the medium.

It is easy to see that as time progresses and energy accumulates a state of instability must arise much the same as that which affects the geyser in the period preceding eruption. Any source of disturbance at this stage may initiate catastrophic breakdown of equilibrium. It may originate in tidal movements gradually augmenting in amplitude as rigidity of the medium diminishes. There will be a critical accumulation of heat which responds to tidal forces to a degree adequate to initiate the breakdown.

When vertical circulation sets in, there can be no break-off till sufficient energy has been discharged to permit of the whole solidifying from beneath upwards and settling down once more into a period of recuperation preceding an ensuing revolution. The depth to which the circulation extends depends upon previous history; *i. e.*, upon the duration of the antecedent storage-period in the great depths. The magnitude of a revolution is so determined.

The phenomena in the geyser and in the substratum are plainly analogous and thermally alike. In the case of the geyser, as in the case of the substratum, there is insufficient loss of heat "from an outer boundary" to control thermal accumulation and consequent instability. Hence it, ultimately, develops cyclic changes analogous to those affecting the substratum. They differ mainly in the nature of the change of state. The refrigerator, too, differs in character. In the one case it is mainly the atmosphere, in the other mainly the ocean which carries away the heat. The like principles affect both. Both appear to be impossible

according to Dr. Jeffreys's statement that cyclic events cannot arise out of a steady thermal supply.

I shall now turn to cyclic phenomena upon a very minute scale—but not the less instructive—arising out of steady thermal flux. I shall first refer to the little device known as an “Air Tester.”

It consists of a thin glass bulb opening into a tube sloping downwards, at the lower end of which there is an upward bend opening into a second small bulb. It is sealed, and contains a small quantity of coloured alcohol or ether. The upper bulb is covered with an absorptive fabric which dips into a vessel containing water ; so that, owing to evaporation, the surface of this bulb is maintained steadily at a lower temperature than that which prevails in the lower bulb with which it communicates.

The alcohol is intermittently drawn up from the lower to the upper bulb, and after a short delay is discharged down the sloping tube into the lower chamber. From this it is again drawn up into the upper bulb, the intermittent motion continuing with perfect regularity so long as the surrounding atmospheric conditions remain unaltered. The influx of heat into the lower bulb and its withdrawal from the upper bulb may be demonstrated by observing the effect of a pad of loose wool applied to either bulb.

We have here a source and a refrigerator. Heat entering into the lower bulb is expended in increasing the vapour-pressure of the alcohol. Heat abstracted from the upper bulb causes a reduction of vapour-pressure. Both effects tend to bring the alcohol, which fits the connecting tube like a piston, into the upper bulb. So soon as it enters the upper bulb the connexion between the bulbs is opened ; there is equalization of pressure throughout, and the alcohol streams back into the lower chamber. Here it fills the bend of the tube, closing the connexion between the two chambers. The difference in vapour-pressure is then re-established, and the phenomena are repeated. Comparing this system with that which is concerned in sustaining the successive revolutions of terrestrial history, we find the development of radioactive heat in the substratum and the change in state of the magma represented by the steady entry of heat into the source and its expenditure in changing the physical state of the working substance. The periodic absorption by the ocean of the accumulated latent heat of liquefaction of the substratum is represented by the periodic condensation and loss of latent heat of the vapour occurring in the refrigerator. There is evidently a physical analogy between the systems.

There is a steady supply of heat entering the system accompanied by cyclical movements of a working substance with and against gravity.

Many years ago, for the purpose of exhibition at a lecture to juveniles on heat-engines, I constructed a simple form of heat-engine of the following kind:—Into a thin glass sphere, about 7 cm. in diameter, a little camphor is introduced. The bulb is then exhausted of air and sealed off. It is next balanced diametrically on pointed trunnions, so that it is free to rotate round a horizontal diameter. A piece of sheet copper is cut to the form of a sector of the sphere. To it is brazed centrally a copper rod, the other end of which can be heated in a Bunsen burner. This sector is separately supported, and can be so arranged as to radiate heat into the sphere either from directly beneath it or in any direction. A screen cuts off the radiant heat of the Bunsen flame.

If we place the radiator directly beneath the axis of rotation, the following effects are produced. The camphor is slowly sublimed and is deposited in brilliant crystals on the inner upper surface of the sphere. This progresses till the camphor has for the most part collected on the upper walls of the bulb. The conditions are then unstable; a small inequality in the distribution of the camphor above causes the bulb to make a half turn, the camphor being brought down into a position immediately over the heater. It is then again evaporated till unstable equilibrium is attained, when there is another half turn. If the bearings are not quite free, and if the whole is shielded from draughts, there may be a long pause, but sooner or later the inversion of the bulb occurs. A slight cross draught shortens the period. Or, by displacing the heater some little way upwards and from immediately beneath the axis of rotation, the same effect is brought about.

Here, again, there is a source and a refrigerator. The motion of the working substance is the result of the vaporization, the absorbed heat becoming latent. Again, we have the analogy of latent heat collected in the substratum till there is change of state, and owing to this change of state the working substance migrating upwards. In the sublimation engine the return movement of the working substance is effected by the rotation of the containing vessel. In the substratum the working substance, owing to its increased density attending solidification, of itself sinks back into the depths. The sublimation engine may be run for hours without attention; the periodic movement of the working substance, from source to refrigerator and again back to the source, in

other words the intermittent discharge of the energy, continuing monotonously. As to the institution of independent and periodic air-currents to shorten the period of unstable equilibrium, we find here the counterpart of periodic tidal intervention whereby the physical breakdown of the energy-laden substratum is accelerated.

The use of the rotating vessel is not essential. It enables a small mass of the working substance to suffice. On a large scale a sufficient accumulation of the sublimed substance upon an overlying refrigerator must of itself break off and descend to the source. This would constitute an experimental reproduction of the substratal conditions in all essential respects; and possibly as good as any we can hope to attain in the laboratory, having regard to the fact that a low-temperature and low-pressure reproduction of the exact working conditions affecting the substratum is clearly impossible: even could we find a suitable working substance.

As already intimated, Dr. Jeffreys's argument in reality only applies to such systems as admit of no movement of the parts of the medium involved. If there is such movement then, attending steady flow of heat, cyclical events may arise and prevail indefinitely. And this is true even in the complete absence of latency.

A simple case of a heat-engine working on such lines is described by E. H. Griffiths*. There are no valves or similar contrivances. A steady thermal source supplies heat to a glass bulb containing air. This bulb makes air-tight connexion with one arm of a U tube partially filled with mercury. The other arm of the U tube is open.

When the temperature of the air in the bulb rises, the mercury in that arm of the U tube with which it is connected is depressed. The entering air cools rapidly, partly because of the work done, partly because of contact with cold surfaces. Accordingly there is fall of pressure, and the mercury again rises in the U tube. A fresh influx of heated air from the bulb then initiates another down-stroke; and so on. Here there is a complete cycle in which more work is done upon the down-stroke than upon the up-stroke, at the expense of the steady thermal supply. The cycles continue indefinitely so long as the thermal supply continues.

This system violates Dr. Jeffreys's statement simply because his statement is not applicable to systems where there exists a working substance; *i. e.*, one which is instrumental in doing

* 'The Thermal Measurement of Energy' (Cambridge, 1906), p. 4 *et seq.*

work at the expense of transported heat received from a steady thermal supply. It is only true of systems in which there are no translatory movements of parts of the medium. It is purely concerned with conductivity, *i.e.* the flux of heat from one part of a medium to another, the medium itself remaining at rest.

In the concluding paragraph of Dr. Jeffreys's statement, quoted from the 'Geological Magazine' (*ante*) and also in his earlier paper in this Journal (Phil. Mag. May 26, 1926), he dwells upon the supposed inadequacy of tidal forces to establish a sufficient displacement of the outer crust of the earth over a molten substratum to effect the discharge of heat accumulated beneath the continents. It is true that in the earlier paper his mathematical investigation of the matter leads him to the result that in this respect the theory may possibly be self-consistent if we assume a molten stratum no more than 20 kms. in depth. Although such a restriction by no means invalidates the theory, as I pointed out at the time (Phil. Mag. May 1926, p. 936 *et seq.*), it would appear that this restriction may have arisen out of his simplifying assumptions.

Dr. Jeffreys writes (*loc. cit.* p. 928):—"Let us then investigate the tides in a thin viscous fluid layer just below the surface. The outer crust is supposed thin enough to offer negligible opposition to the motion of the fluid, so that the upper boundary of the fluid will be treated as free." We must infer from this, as well as from the succeeding analysis, that Dr. Jeffreys discards the effects of the compensations of the continents in interfering with tidal movements in a fluid substratum.

Several eminent mathematicians have discussed the question of the movement of the outer crust of the earth over the interior as arising out of oceanic tides—a movement which must result in lengthening the day by a little

Prof. Eddington has discussed this matter in a recent suggestive address to the Geological Society ('Nature,' Jan. 6th, 1923). He considers the effects of the arrestment of oceanic tidal movements by surface obstacles upon the outer crust of the earth. It is well known, as arising out of the work of Taylor and its extension by Jeffreys, that the dissipation of oceanic tidal energy is mainly accounted for by turbulent motions taking place in certain quite unrestricted areas where the land interferes with tidal translatory movements. Eddington discusses the effects of such interference as, possibly, in a minute degree lengthening the day, even under existing conditions of the substratum. "The frictional

dissipation acts as a brake on the earth's rotation, and we now feel confident that the brake is a surface brake applied at certain points on the earth's surface where the favourable conditions exist. The retarding force is transmitted into the earth's interior and so delays the rotation as a whole ; but unless the material is entirely non-plastic there will be a tendency for the outer layers to slip over the inner layers." He discusses the effects of a minute and variable slipping of the whole crust from east to west over the main part of the interior as helpful in explaining irregularities in the motions of heavenly bodies etc.

Professor Love refers to such effects. In a well-known paper of his (*Proc. R. S. A.* vol. lxxxii. p. 73), "On the Yielding of the Earth to Disturbing Forces," he refers to certain consequences which must ensue if a fluid layer intervenes between the outer and inner regions of the earth. Such a layer, having regard to the existing rigidity of the earth, involves an impossible rigidity of the outer enclosing shell. Molten matter might exist in isolated areas, but cannot form a continuous sheet separating a central body from an enclosing crust. "The conclusion does not negative the possible existence of a layer of comparatively small rigidity ; but if there is such a layer, it must be rigid enough to prevent the finite slipping of the enclosing crust over the central body."

Professor Larmor, in a recent number of 'Nature' (Sept. 11, 1926), refers to this subject. A deep sub-crustal layer in a condition of fluidity is not compatible with the existence of the actual oceanic tides. The lagging tidal pull, if large enough, might cause a westward drift of the fluid surface material as a whole. The principle of Archimedes must assert itself so that there would be no differential effect on the floating continents and mountain ranges—"except in so far as a uniform drift may be obstructed or deflected locally by the more solid roots of the floating continents that are carried along with it."

Here the statement regarding the effect of the Archimedean principle, while, of course, essentially true, seems to leave out of account an ultimate effect arising out of the vertical separation of the centre of gravity of the floating continents from the centre of buoyancy.

Attending the coming into existence of a molten substratum, oceanic tides would cease or be greatly reduced. But the interference of the continents would then be transferred to their compensations "in so far as a uniform drift may be obstructed or deflected locally by the more solid

roots of the floating continents that are carried along with it."

It would appear that Dr. Jeffreys's simplifying assumption—although for mathematical reasons possibly unavoidable—must result in depriving his final conclusion of the significance which he attaches to it. The limitations he deduces have, in fact, been introduced by his own assumptions, which have led him to omit important factors concerned in the genesis of a general shift of the outer crust over the inner parts of the surface of the earth. At times when the existing rigid substratum is replaced by a mobile fluid, the energy of tidal movements prevailing in it becomes more or less dissipated locally in turbulence among the downward-reaching compensations of the continents. The reactionary effect upon the whole outer crust—continents and ocean-floor—is inevitable, and certainly cannot be ignored.

XXXII. *On the Large Bending of Thin Flexible Strips and the Measurement of their Elasticity.* By F. H. HUMMEL, M.Sc., and W. B. MORTON, M.A., Queen's University, Belfast*.

§ 1. **T**HE ordinary formulæ which are used when Young's modulus is measured by the bending of straight bars, under an attached load or under their own weight, are limited in their application to cases where the deflexions from the horizontal are small in comparison with the length of the bar. This limitation gives rise to practical difficulties in dealing with very flexible strips, such as a ribbon of thin steel. It seems worth while, therefore, to examine the problem of the large bending of such a strip and, incidentally, the limits within which the approximate formulæ can be used. When the weight of the strip is negligible in comparison with the attached load, the exact solution can be expressed by elliptic functions, but for the bending caused by the weight of the strip itself a method of approximation has to be sought.

The mathematical analysis can be made neater by the introduction of a "characteristic load" in the first problem and a "characteristic length" in the second. For a strip of given length, cross-section, and material the magnitudes l , E , and I determine a force $El/l^2 = P$, say, irrespective of the weight of the strip. On the other hand, if w is the

* Communicated by the Authors.

weight per unit length, the length $(EI/w)^{\frac{1}{2}} = c$, say, is characteristic of the strip whatever be its length. The bending of a weightless strip is determined by the ratio of the attached load to P , and that of a strip under its own weight by the ratio of its length to c , and the symbols EIw disappear from the analysis.

In each case we suppose the strip to be clamped horizontally at one end. The origin is at this end, xy being measured horizontally and vertically downwards. The inclination of the tangent at any point is denoted by ϕ , and its maximum value at the outer end by α .

§ 2. Strip of negligible weight bent by terminal load.

The following results are taken from the theory of the "elastica." The coordinates and the length are expressed by the aid of an auxiliary length, a , and an auxiliary angle, χ , defined by $a = l(P/W)^{\frac{1}{2}}$, where W is the load and P the characteristic load as above defined:

$$\sin \chi = \sin \frac{\pi}{4} \left/ \sin \left(\frac{\pi}{4} + \frac{1}{2} \phi \right) \right.,$$

where ϕ is the inclination of the tangent at the point.

Then

$$x = 2a \sin \left(\frac{\pi}{4} + \frac{1}{2} \alpha \right) \cos \chi,$$

$$y = a \{ (K - F\chi) - 2(E - E\chi) \},$$

with the usual notation of Legendre's functions, the modulus of which is $\sin \left(\frac{\pi}{4} + \frac{1}{2} \alpha \right)$,

$$l = a(K - F\chi).$$

On elimination of a we have

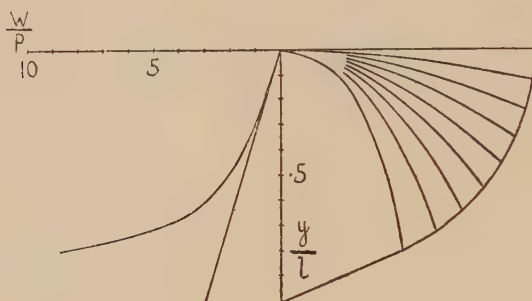
$$x/l = 2 \sin \left(\frac{\pi}{4} + \frac{1}{2} \alpha \right) \cos \chi / (K - F\chi),$$

$$y/l = 1 - 2(E - E\chi) / (K - F\chi).$$

At the terminal point $\phi = \alpha$. Having calculated the corresponding coordinates for a succession of values of α , we can plot the locus described by the end of the strip as the load is continually increased.

The result is shown on fig. 1, where the forms of the rod for $\alpha = 5^\circ, 10^\circ, \dots, 40^\circ$ have also been drawn. It will be seen that the locus makes a finite angle with the horizontal at the lowest point, corresponding to infinite load.

Fig. 1.



It is not hard to show that this angle is $\pi/8$.

$$\begin{aligned} \text{For as } \alpha &\longrightarrow \pi/2, \\ \chi &\longrightarrow \pi/4, \\ \text{the modulus} &\longrightarrow 1, \\ E\chi &\longrightarrow \sin \chi; \end{aligned}$$

therefore

$$(l-y)/x = (E-E\chi)/\sin\left(\frac{\pi}{4} + \frac{1}{2}\alpha\right)\cos\chi \longrightarrow \sqrt{2}-1 = \tan \pi/8.$$

On the other side of the vertical are plotted the loads corresponding to the vertical deflexions, expressed as multiples of P . The straight line which touches this graph at the origin shows the loads which would be calculated on the elementary formula,

$$W/P = 3y/l.$$

It will be seen that the agreement is quite good until the drop is about one-quarter of the length of the strip.

A simple relation connects the force P with the horizontal coordinate of the end of the strip and the terminal inclination under given load W .

We have

$$\begin{aligned} P &= Wa^2/l^2 = W/(K-F\chi)^2 \\ &= Wx^2/4l^2 \sin^2\left(\frac{\pi}{4} + \frac{1}{2}\alpha\right)\cos^2\chi. \end{aligned}$$

In this χ has the value corresponding to $\phi = \alpha$.

$$\text{So} \quad \sin^2 \chi = 1/2 \sin^2 \left(\frac{\pi}{4} + \frac{1}{2} \alpha \right),$$

$$P = W x^2 / 2l^2 \sin \alpha,$$

$$\text{and} \quad EI = Pl^2 = W x^2 / 2 \sin \alpha.$$

If the strip is so much bent that α approaches $\pi/2$, this result gives $EI = \frac{1}{2} W x^2$ very nearly.

§ 3. *Bending of a strip under its own weight.*

Let s be the arc measured from the free end. The equation of moments for the element ds gives the differential equation

$$EI d^2 \phi / ds^2 = -ws \cos \phi.$$

When the characteristic length c is introduced, this becomes

$$d^2 \phi / ds^2 = -s \cos \phi / c^3.$$

The equation is further simplified by taking as independent variable the ratio $\sigma = s/c$; we have then

$$d^2 \phi / d\sigma^2 = -\sigma \cos \phi.$$

Let us try if this can be satisfied by an expansion of ϕ in powers of σ .

$$\text{Put} \quad \phi = \alpha + A_2 \sigma^2 + A_3 \sigma^3 + \dots,$$

in which account has been taken of the terminal conditions $\phi = \alpha$, $d\phi/ds = 0$ when $\sigma = 0$.

Inserting in the equation and disregarding questions of convergency, we get

$$\begin{aligned} 1.2 A_2 + 2.3 A_3 \sigma + \dots \\ = -\sigma \{ \cos \alpha - \sin \alpha (A_2 \sigma^2 + A_3 \sigma^3 + \dots) \\ - \frac{1}{2!} \cos \alpha (A_2 \sigma^2 + A_3 \sigma^3 + \dots)^2 + \dots \}. \end{aligned}$$

On equating coefficients it is found that the only A 's which do not vanish are those whose indices are multiples of three; and each of these is expressed in terms of those preceding it. Thus

$$2.3 A_3 = \cos \alpha,$$

$$5.6 A_6 = \sin \alpha A_3^3,$$

$$8.9 A_9 = \sin \alpha A_6 + \frac{1}{2} \cos \alpha A_3^2,$$

and so on, the connecting equations becoming rapidly more complicated as the higher powers in the multinomial expansions are taken. If we change the notation and write

B_1 for A_3 , B_2 for A_6 , and so on, then B_n is a homogeneous function of degree n in $\sin \alpha$ and $\cos \alpha$. For purposes of computation it is convenient to transform these into expressions involving sines and cosines of multiples of α . We find sines of even multiples or cosines of odd multiples according as n is even or odd.

The first six expressions are :

$$B_1 = -\cos \alpha/2 \cdot 3,$$

$$B_2 = -\sin 2\alpha/2^3 \cdot 3^2 \cdot 5,$$

$$B_3 = (13 \cos \alpha + 7 \cos 3\alpha)/2^3 \cdot 3^4 \cdot 5,$$

$$B_4 = (94 \sin 2\alpha + 51 \sin 4\alpha)/2^{11} \cdot 3^5 \cdot 5 \cdot 11,$$

$$B_5 = -(6922 \cos \alpha + 7519 \cos 3\alpha + 3159 \cos 5\alpha) / 2^{13} \cdot 3^6 \cdot 5^3 \cdot 7 \cdot 11,$$

$$B_6 = -(160963 \sin 2\alpha + 169560 \sin 4\alpha + 59439 \sin 6\alpha) / 2^{15} \cdot 3^8 \cdot 5^3 \cdot 7 \cdot 11 \cdot 17.$$

Assuming that a sufficiently accurate value can be obtained from a small number of terms of the series in any given case, we can proceed as follows. Putting $\phi = 0$ and solving the resulting equation for σ by successive approximations, we find the length of strip which, clamped horizontally at one end, will droop so that the slope is α at the other end. The root of the equation is the ratio of this length l to the characteristic length c . Suppose the series to be convergent for the assumed σ and for values of σ up to l/c . We now compute ϕ for a number of values of σ in this range, and tabulate $\cos \phi$ and $\sin \phi$. The coordinates of a point on the strip are given by

$$x = c \int_{\sigma}^{l/c} \cos \phi \, d\sigma,$$

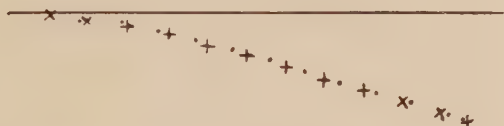
$$y = c \int_{\sigma}^{l/c} \sin \phi \, d\sigma.$$

By using an integraph the graphs of x/c , y/c against σ can be obtained from those of $\cos \phi$, $\sin \phi$, and then the form of the strip is got by plotting together corresponding values of xy .

A comparison with experiment was made by using a strip of pen-steel of length 12 inches. Measurements of (xy) were made at horizontal intervals of an inch, and the terminal slope was found to be $17^\circ 40'$ approximately. When this value is taken for α the ratio l/c comes out to be 1.249; so in order to compare the observed values of the coordinates with those calculated by the method above described, the former are to be multiplied by the factor $1.249/12 = .104$.

The points so obtained are marked with a cross on fig. 2; the points marked with a dot are those obtained by calculation. For purposes of measurement we require merely the co-ordinates of the end-point of the strip. It is then better

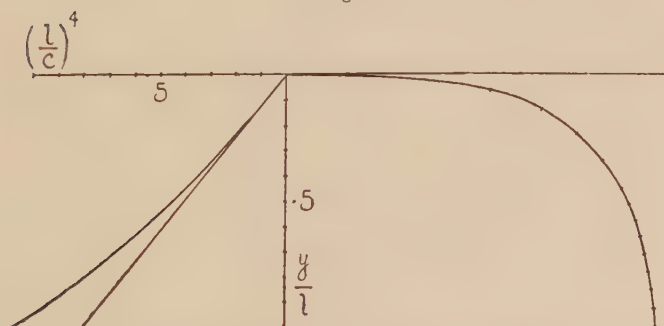
Fig. 2.



to use arithmetical quadrature which can be pushed to any desired degree of accuracy. The process has been carried out for values of α at intervals of 5° from 5° to 45° , with an interval of 0.1 for σ .

The results are shown in the first four columns of the

Fig. 3.



following table, and fig. 3 is the locus described by the end-point as the strip is paid out through the clamp:—

α .	l/c .	x/c .	y/c .	$\frac{1}{8}(6\alpha)^{\frac{3}{2}}$.
5°	·806	·802	·053	·053
10°	1·018	1·008	·133	·133
15°	1·170	1·144	·228	·228
20°	1·298	1·248	·336	·335
25°	1·408	1·322	·452	·451
$27\frac{1}{2}^\circ$	1·460	1·353	·513	·512
30° ..	1·512	1·381	·576	·575
$32\frac{1}{2}^\circ$	1·562	1·402	·641	·640
35°	1·612	1·421	·709	·706
$37\frac{1}{2}^\circ$	1·660	1·434	·778	·775
40°	1·711	1·448	·850	·844
$42\frac{1}{2}^\circ$	1·762	1·456	·924	·915
45°	1·811	1·461	·998	·987

On the other side of the vertical are plotted the values of $(l/c)^4$ to show the departure from the linear relation $(l/c)^4 = 8y/c$ given by the elementary formula.

We have not been able to make any headway with the analytical investigation of the convergency of the series, and so have had to be content with an arithmetical treatment and experimental verification. This is very unsatisfactory from a mathematical point of view, but is perhaps sufficient for practical purposes. It is pretty obvious that the series is convergent for $\sigma < 1$, but it will be seen from the table that this does not carry us to the clamped end, even for $\alpha = 10^\circ$. When the computation is made to include four decimal places, it is found that three terms suffice up to $\alpha = 20^\circ$. For the highest values of σ , a fourth term has to be taken into account from 20° to 35° and a fifth for 40° and 45° .

§ 4. *Measurement of Elasticity.*

The theory given above can be made available in several ways for the measurement of Young's Modulus. There is an obvious practical advantage in using the bending due to the weight of the strip itself, which perhaps outweighs the unsatisfactory nature of its mathematical basis. For the sake of completeness both cases will be taken together; in each case three different methods may be suggested.

(1) By the coordinates of the end-point. This is the plan followed in the application of the elementary formula to small bending. If we use the vertical drop, y , a graph can be plotted with y/l as abscissa, and as ordinate the ratio of the characteristic force to the actual load, or the characteristic length to the length of the strip, P/W or c/l respectively. These graphs are shown on fig. 4.

(2) By the slope of the chord. For a definite value of P/W in the first case, c/l in the second, the line joining the clamped end to the loaded or free end has a definite inclination to the horizontal. By graphical interpolation the values of the terminal y/x can be found which correspond to a range of values of the ratios in question. If a set of lines be drawn on a vertical sheet placed behind the strip, radiating from the point where the end is clamped (fig. 5), we have only to adjust the load or push the strip through the clamp until its tip lies on one of the lines. Multiplication of W or l by the corresponding factor then gives P or c . Of course the measurements of the former kind will be subjected to the usual inaccuracy if the weight of the strip is not negligible compared with W .

(3) By the terminal slope of the strip. This is a very practicable and convenient way; the strip is nearly straight

Fig. 4.

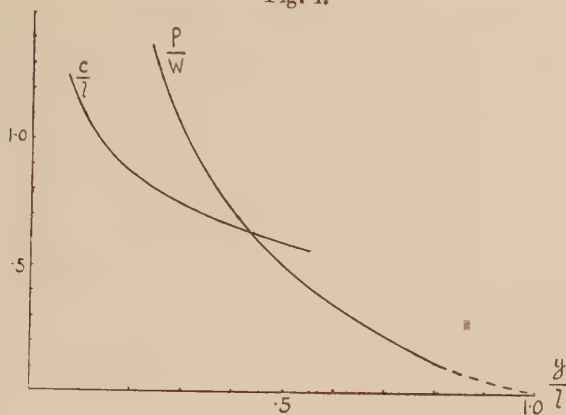


Fig. 5.

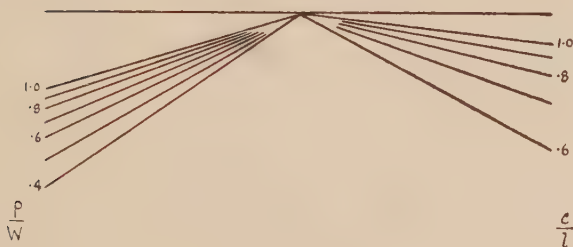
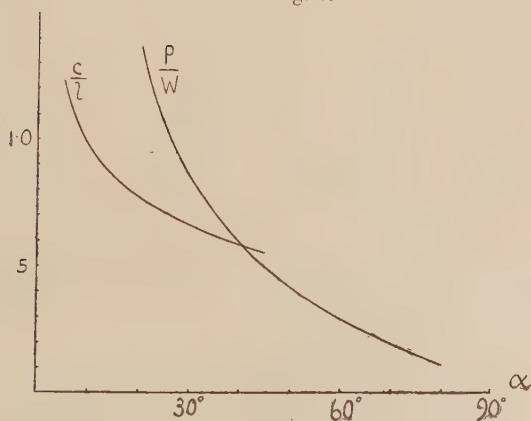


Fig. 6.



for some distance from its end, so that it is easy to set a straight edge parallel to it, or to adjust it to be parallel to a set of lines ruled on a vertical sheet. The connexion between the ratios and the end-slope is shown on fig. 6.

The following numbers show the results of some measurements made by this method, using a strip of pen-steel bent by its own weight. No special refinements were attempted to secure accuracy. A bracket of angle-iron was fastened at an upper corner of a vertical drawing-board with one of its faces horizontal. The strip was clamped on this face by laying a heavy weight on it. The face was adjusted by a spirit-level. In the first set of readings the end-slope was measured for an even length of strip, and the factor was read off the graph; in the second the length was adjusted so as to give, at the end, one of the special inclinations in the first column of the table of § 3 for which the reciprocal of the ratio is given in the second column.

By measured end-slopes :—

α .	l .	c/l .	c .
14° 30'	12 in.	·862	10·34 in.
22° 0'	14	·742	10·39
31° 0'	16	·650	10·40
40° 40'	18	·580	10·44
Average ...			10·39

By adjusted end-slopes :—

α .	l .	c/l .	c .
15°	12·16 in.	·854	10·38 in.
20°	13·52	·771	10·40
25°	14·72	·711	10·46
30°	15·78	·661	10·42
35°	16·90	·610	10·30
40°	17·86	·584	10·42
45°	18·84	·551	10·36
Average ...			10·39

The dimensions of the section of this strip were 0·635 in. by 0·0117 in., and its weight per inch 0·00210 lb. This gives $E = 2·78 \times 10^7$ lb. per sq. in.

Two curious accidental results may be noticed here which may be used to get approximate values for the characteristic length without using the table or graph. The first is the fact that y is very nearly identical with c when the end-slope is 45° (see table). So to find c it is only necessary to pay out

the strip until the end is parallel to the hypotenuse of a 45° set-square and then measure the vertical drop at the end. The second is found when we extrapolate the relation existing, for small bending, between the drop and the circular measure of the end-slope. We have then

$$y = wl^4/8EI = l^4/8c^3,$$

$$dy/dx = \alpha = wl^3/6EI = l^3/6c^3;$$

on elimination of l ,

$$y/c = \frac{1}{8}(6\alpha)^{\frac{4}{3}}.$$

When this formula is extended to the range of α included in the table, the fifth column is obtained. Comparison with the fourth column shows a close agreement, so that an approximate value of c can be got from measurement of $(y\alpha)$ by use of the formula. None of the other relations, holding between the various magnitudes in the limit of small bending, can be extrapolated to this extent without large errors.

In conclusion, a few results of experience on the experimental side may be added. The end-slope should not be less than about 15°. Each determination should be repeated with the strip turned over and a mean taken. This eliminates the effect of any slight permanent curvature which the strip may have. The experiments showed that such curvature is generally present, and it cannot be corrected by manipulation of the strip. A convenient way of attaching a weight is to make two very small nicks with a file in the sides of the strip near the end. A loop of thread carrying the weight is then passed round the side nicks and brought over on the top side to hang clear from the end of the strip.

As regards approach to the elastic limit, it is to be remembered that the maximum extension and compression are of the order of the half thickness of the strip divided by the radius of curvature; so with a thin strip the strains are small, even with considerable bending.

XXXIII. *The Surface-Tension Balance.* By E. L. WARREN,
*Student in Physics at the Royal College of Science, South
 Kensington* *.

[Plate VI.]

THE determination of the surface-tension of liquids by the capillary ascent method is by no means susceptible to the accuracy usually attributed to it. It is difficult, in the first place, to find a capillary tube of sufficiently uniform cross-section, and when one has been found, the calibration, cleaning, and keeping clean of this tube are no small matters. Moreover, difficulty is experienced in measuring accurately the height of ascent of the liquid in the tube. Furthermore, elaborate thermostatic arrangements are necessary in order to estimate with precision the temperature of the meniscus, and, in consequence, this method is not suitable for the investigation of the variation of surface-tension with temperature. Finally, when every precaution has been taken to overcome these difficulties, it must be remembered that the result obtained represents $T \cos \theta$, where T is the surface-tension and θ the contact angle between the liquid and the walls of the tube, and not simply T . The value of the contact angle is very uncertain: *e.g.*, the value of the contact angle between glass and water is stated by Quincke to be $8-9^\circ$, but by Wilberforce to be 0° . The latter observer used especially clean glass. Seeing that it is impossible to be absolutely sure that the inside of a capillary tube is perfectly clean, the contact angle which actually exists during an experiment may have any value from 0° to 9° , or even greater. Hence an error of possibly more than 1 per cent. may be introduced.

Surface-tension measurements play an important part in modern colloidal work, and for this reason it has become necessary that methods for their determination should be developed which are accurate, rapid, and do not make too great a demand on the instrumental equipment of a technical laboratory. The capillary-ascent method certainly does not satisfy these requirements.

A knowledge of the variation of surface-tension with temperature is of considerable importance. Dr. Ferguson † has stated that the variation of the surface-tension of unassociated liquids with temperature can be expressed very accurately from its freezing-point to its critical temperature

* Communicated by Prof. H. Gregory, Ph.D.

† Ferguson, *Phil. Mag.*, Jan. 1916, p. 37.

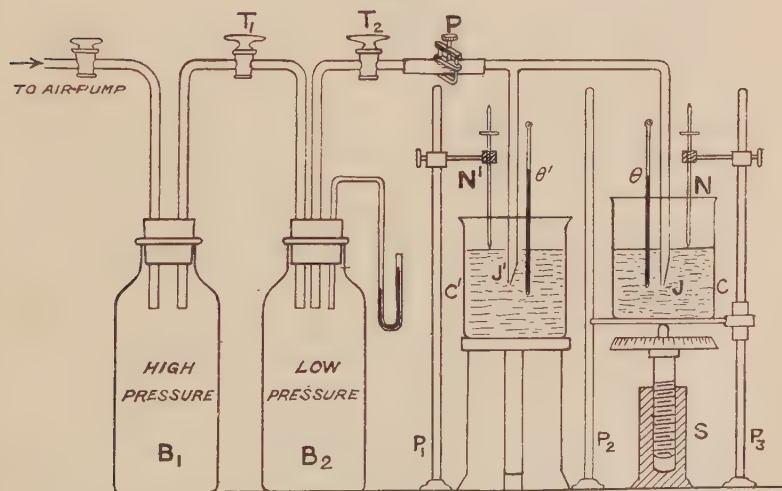
by the equation $T_\theta = T_0(1 - b\theta)^n$, where T_0 and T_θ are the surface-tensions of the liquid at the temperatures 0 and θ respectively, and b the reciprocal of the critical temperature. n is constant for any one liquid. Obviously, then, if we take accurate measurements of the surface-tension of an unassociated liquid over a fairly wide range of temperature, we can calculate b and n , and from b the critical temperature of the liquid.

The method to be discussed is a modification of Jaeger's method, and has been designed primarily for the experimental determination of the temperature-coefficient of surface-tension, and for the investigation of the dependence of the surface-tension of solutions on their concentration. The chief feature of the method is that it enables all such measurements to be expressed in terms of the surface-tension of some appropriate standard liquid such as water.

Description of the Surface-Tension Balance.

The apparatus (see fig. 1) consists of two small circular jets J and J' of the same cross-section, which are in gaseous

Fig. 1.



connexion with each other and with the bottle B_2 . The jets are immersed in liquids in the beakers C and C'. The air in the bottle B_2 is maintained at a pressure of a few millimetres of mercury above that of the atmosphere. The pinch-cock P is opened until bubbles of gas escape at intervals of

about five seconds from one of the jets. The depth of immersion of the jet J is adjusted until the bubbles escape approximately alternately from the two jets. This arrangement enables the surface-tension of the liquid in the beaker C to be balanced against that of the liquid in the second beaker C'. The balance is independent of the pressure maintaining the bubble system. In order that this may be so it is essential that the two jets should be identical in size and shape.

Preparation and Calibration of the Jets.

A piece of ordinary glass tubing about 20 centimetres long was heated in the centre, drawn out until it measured about one millimetre in diameter, and cut into two sections at its narrowest point. In this way, seeing that each orifice was represented by one side of the break, two exactly similar jets were obtained. Many pairs of jets were made before two were obtained which were sufficiently circular, and in the preparation of which the tube had broken in a clean manner in a plane approximately perpendicular to the axis of the tube. The jets finally selected were such that the greatest difference between any two diameters was less than 1 per cent. A difference of as much as 2 per cent. in any two diameters would make a difference of only 1/100 per cent. in the value of the surface-tension.

The mean diameter of each orifice was determined separately. Measurements were taken across six diameters, at orientations increasing by 30° , by means of the cathetometer microscope, used to measure the variation of the depths of immersion of the jets. The values obtained for the mean diameters of the two jets were 1.2123 and 1.2111 millimetres respectively, which, to the degree of accuracy of the measurements, are identical.

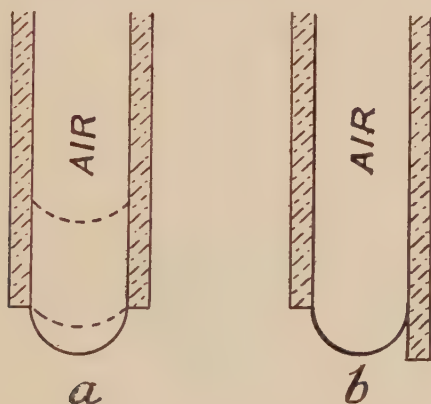
The two jets are clamped vertically in a horizontal steel bar bolted to the tops of the steel pillars P_1 , P_2 , and P_3 .

Formation of the Bubbles.

The air in the bottle B_1 is raised to a pressure of a few centimetres of mercury above that of the atmosphere, and the tap T_1 is opened until the manometer in communication with the second bottle registers a pressure of a few millimetres of mercury in excess of atmospheric pressure. On opening the tap T_2 , the pinchcock P being in adjustment, the meniscus in each tube will be forced slowly down until a bubble is

formed at one of the orifices and escapes. While the meniscus is moving down the interior of the jet its shape will remain the same, but when it reaches the orifice the bubble will slowly increase in size until the section of the meniscus in contact with the edge of the orifice is vertical (see fig. 2*a*). The pressure on the concave side of the meniscus being greater than on the convex side, further increase in the size of the bubble causes it to become unstable and break away from the jet. The meniscus then takes up a position in the tube about three or four centimetres above the orifice, and a new bubble commences to form,

Fig. 2.



Hence the escape of the bubble causes a slight decrease in the level of the free surface of the liquid. This diminution is equal to about $4 \times \frac{r^2}{R^2}$ millimetres, where r and R are the radii of the orifice and beaker respectively, and is, except where extreme accuracy is required, negligible.

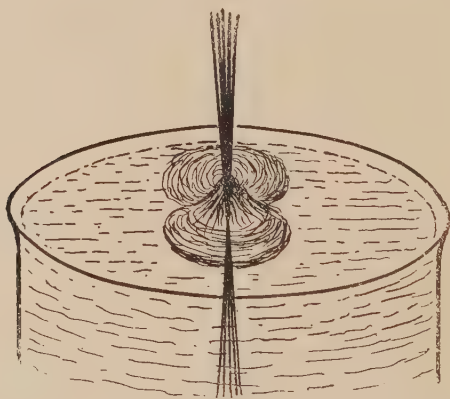
No matter what the contact angle between the liquid and the glass may be, the bubble cannot become unstable until the edge of the meniscus is vertical. If the plane of the orifice is not horizontal, the axis of the jet however being vertical, the shape of the bubble will not be affected, but the effective immersed depth will be equal to the depth of the highest point of the edge of the orifice below the free surface of the liquid (see fig. 2, *b*).

*Adjustment and Measurement of the Depth of Immersion
of the Jets.*

The jet J' is immersed to a depth of two or three centimetres in a suitable liquid in the beaker C' resting on a rigid wooden support. The jet J is immersed in a second liquid in the beaker C . This rests on a metal platform which is capable of sliding up between the two vertical steel pillars P_2 and P_3 . The platform may be moved in a vertical direction by means of a screw S of small pitch. In this way the depth of immersion of the jet may be adjusted with great precision.

This being accomplished, the depth of immersion may be measured with the aid of the screw-pin N . The latter consists of a screw of small pitch terminated at each end by a sharp nickel point. The screw moves vertically through a bracket capable of sliding up the pillar P_3 .

Fig. 3.



On illuminating the surface of the liquid from a large angle of incidence, and viewing the surface in the direction of the reflected rays, the surface appears to be flooded with light. While viewing the surface in this manner the image of the pin can be seen distinctly, and the pin is slowly screwed down until the pin and its image meet. This adjustment may be made with great accuracy, for immediately the pin touches the surface of the liquid a dark patch appears round the point of the pin, due to the curvature of the surface in its vicinity caused by the slight ascent of the liquid up the sides of the pin (see fig. 3). On removing the beaker C the distance from the lower point of the pin and the orifice may

be measured by means of a cathetometer microscope. The depth of immersion of the jet J' is measured in precisely the same manner.

There are two ways of determining the surface-tension of a liquid with the Surface-Tension Balance, viz.:—

1. A suitable liquid of which the surface-tension is known and the liquid under investigation are placed in the beakers C' and C respectively. The balance is set and the depths of immersion of the two jets are measured. The surface-tension of the liquid under investigation can then be calculated.

2. Any convenient liquid is placed in the beaker C' . The liquid under investigation is placed in the beaker C , the balance is set, and the pin N is screwed down until it touches the free surface of the liquid. A cathetometer microscope is set on the upper point of the screwpin. The liquid under investigation is replaced by the standard liquid, the balance is again set, and the pin N readjusted. The movement of the pin is measured by means of the cathetometer microscope. The depth of immersion of the jet with respect to the standard liquid is then measured. Then, if h_1 is the immersed depth with respect to the standard liquid, and x the movement of the pin, the downward sense being counted positive, the immersed depth with respect to the liquid under investigation is equal to $(h_1 + x)$.

If the movement of the pin is small compared with the immersed depth, and is measured accurately, an error of 1 per cent. in the measurement of the immersed depth only

involves an error of approximately $\left(\frac{\rho_s - \rho}{\rho}\right)$ per cent., where

ρ and ρ_s are the densities of the liquid under investigation and the standard liquid respectively. This method is that used for measuring the variation of the surface-tension of liquids with temperature, for in this case the liquid under investigation at a certain temperature is adopted as the

standard, and hence $\left(\frac{\rho_s - \rho}{\rho}\right)$ is very small compared with

unity : *e.g.*, for water from 0° $\left(\frac{\rho_s - \rho}{\rho}\right)$ per cent.
is less than 0.04 per cent.

In order to measure the temperature of the meniscus, a thermometer graduated to tenths of centigrade degrees was suspended in each liquid, so that its bulb was less than one millimetre from the orifice.

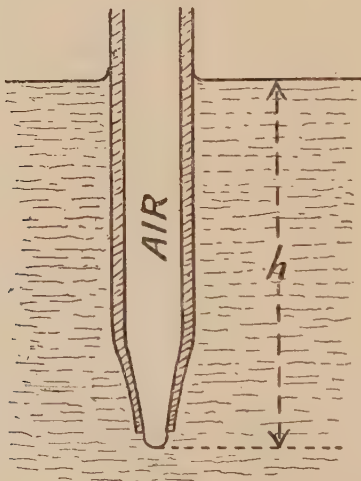
The Surface-Tension Balance is especially suitable as compared with the capillary-rise method for measuring the

surface-tension of solutions. In the latter method the liquid has to pass into a glass tube of which the walls are not perfectly clean and contamination by the dirt or adsorption by the walls of the tube is probable. When the Surface-Tension Balance is used, the breaking away of the bubbles and consequent sudden rush of the solution into the jet ascertains that the jet is kept clean and the solution of uniform strength.

Theory of the Method.

Consider a tube tapering down to an orifice of about one millimetre diameter immersed with its axis vertical in a

Fig. 4.



liquid of density ρ (see fig. 4). Let the pressure of the air in the tube be gradually increased until a bubble is formed at the orifice and is just on the point of breaking away. When this is the case, the edge of the meniscus then being vertical, the meniscus is identical in shape with that due to the capillary ascent of a liquid of zero contact angle in a narrow tube. Let the depth of the apex of the bubble below the surface of the liquid be h . The pressure P_i on the concave side of the meniscus is given by

$$P_i = P + g\rho h + \frac{2T}{R}, \quad . \quad . \quad . \quad (1)$$

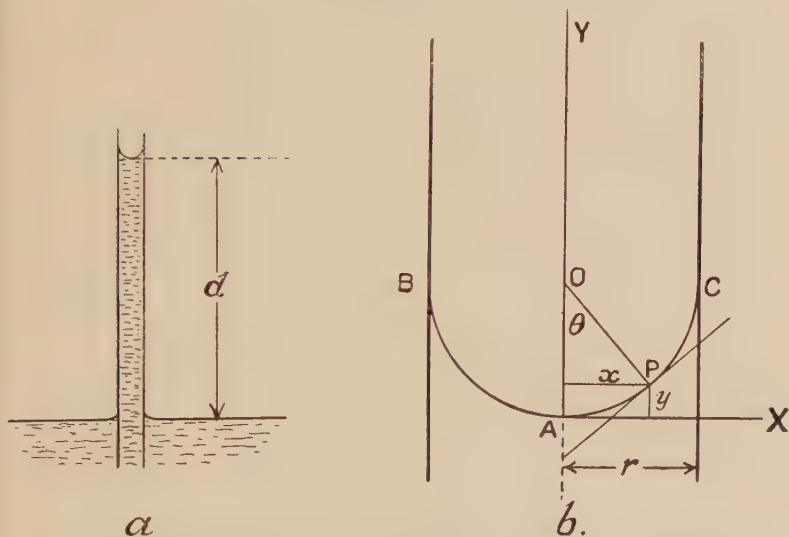
where T is the surface-tension of the liquid, R the radius of

curvature of the meniscus at the vertex, and P the atmospheric pressure.

Consider the capillary-ascent of the liquid in a tube whose radius is equal to that of the orifice. Let us assume that the angle of contact between the liquid and the walls of the tube is zero.

Let fig. 5 (a) represent the liquid in its tube and fig. 5 (b)

Fig. 5.



an enlarged diagram of the surface. The excess of the pressure on the concave side over that on the convex side at the point P is equal to $T \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$, where R_1 is the radius of curvature at P of the curve BAC , and R_2 is the length OP of the normal at P , from its point of intersection O by the Y axis, to the surface.

This pressure excess is also equal to $g\rho(y+d)$, where d is the height of ascent of the liquid in the capillary tube, and y is the vertical distance of the point P above the vertex of the meniscus.

Therefore

$$g\rho(y+d) = T \left(\frac{1}{R_1} + \frac{1}{R_2} \right).$$

Writing the specific cohesion a^2 for $\frac{T}{g\rho}$,

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{y+d}{a^2}.$$

Therefore

$$\frac{1}{x} \frac{d}{dx} (x \sin \theta) = \frac{y+d}{a^2}.$$

The exact solution of this equation is apparently impossible. Approximate solutions have been given by many mathematicians. Poisson * stated that

$$2a^2 = rd \left(1 + \frac{1}{3} \frac{r}{d} - 0.1288 \frac{r^2}{d^2} \right),$$

Mathieu † that

$$2a^2 = rd \left(1 + \frac{1}{3} \frac{r}{d} - \frac{1}{9} \frac{r^2}{d^2} + \dots \right),$$

and Rayleigh ‡, who performed his calculations to a higher degree of accuracy, that

$$2a^2 = rd \left(1 + \frac{1}{3} \frac{r}{d} - 0.1288 \frac{r^2}{d^2} + 0.1312 \frac{r^3}{d^3} \right).$$

The equation

$$2a^2 = rd \left(1 + \frac{1}{3} \frac{r}{d} - 0.1288 \frac{r^2}{d^2} \right) \quad . \quad . \quad . \quad (2)$$

is sufficiently accurate for experimental purposes. At the vertex of the meniscus we have

$$\frac{2T}{R} = g\rho d,$$

$$2a^3 = Rd. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From equations (2) and (3)

$$R = r \left(1 + \frac{1}{3} \frac{r}{d} - 0.1288 \frac{r^2}{d^2} \right). \quad . \quad . \quad . \quad (4)$$

From (2) to a first approximation

$$\frac{1}{d} = \frac{r}{2a^2},$$

and to a second approximation

$$\frac{1}{d} = \frac{r}{2a^2} \left(1 + \frac{1}{3} \frac{r}{d} \right),$$

$$\frac{1}{d} = \frac{r}{2a^2} \left(1 + \frac{r^2}{6a^2} \right).$$

* Poisson, 'Nouvelle Théorie de l'Action Capillaire' (1831), Chap. IV.

† Mathieu, 'Théorie de la Capillarité' (1883), Chap. II.

‡ Rayleigh, Proc. Roy. Soc. (A), xcii. p. 184 (1915).

Substituting the more exact value of $\frac{1}{a}$ in the second term and the more approximate value in the third term of equation (4), we have

$$R = r \left(1 + \frac{r^2}{6a^2} + \frac{r^4}{36a^4} - 0.1288 \frac{r^4}{4a^4} \right),$$

$$R = r \left(1 + \frac{r^2}{6a^2} - 0.0044 \frac{r^2}{a^4} \right),$$

or to a sufficient degree of accuracy

$$R = r \left(1 + \frac{r^2}{6a^2} \right).$$

Equation (1) can now be written

$$(P_i - P) - g\rho h = \frac{2T}{r \left(1 + \frac{r^2}{6a^2} \right)}.$$

Let $(P_i - P) = X$.

Then

$$T = (X - g\rho h) \frac{r}{2} \left(1 + \frac{r^2}{6a^2} \right),$$

or

$$T = (X - g\rho h) \frac{r}{2} + (X - g\rho h) \frac{r^3 \rho g}{12T} \dots \quad (5)$$

To a first approximation

$$(X - g\rho h) = \frac{2T}{r}.$$

Substituting this value in the second term of equation (5), we have

$$T = (X - g\rho h) \frac{r}{2} + \frac{1}{6} g\rho r^2, \quad \dots \quad (6)$$

where X denotes the excess pressure in the bottle B_2 over that of the atmosphere.

Equation (6) is applicable to the double-jet system described above.

Let r denote the radius of the jets.

Let ρ and T denote the density and surface-tension of the liquid in the beaker C , and h the distance from the surface of this liquid to the vertex of the meniscus when the bubble is about to break away from the jet J . Let ρ' , T' , and h' be the corresponding quantities for the liquid in the beaker C' .

Then from (6)

$$T = (X - g\rho h) \frac{r}{2} + \frac{1}{6} g\rho r^2,$$

$$T' = (X - g\rho' h') \frac{r}{2} + \frac{1}{6} g\rho' r^2.$$

Hence, by subtraction

$$T - T' = g \frac{r}{2} (\rho' h' - \rho h) + \frac{1}{6} g r^2 (\rho - \rho'). \quad . \quad . \quad (7)$$

Hence, if we know T' we can measure r , h , ρ , h' , and ρ' , and then calculate the value of T .

If we replace the liquid in the beaker C by another liquid of which the quantities corresponding to ρ , h , and T are ρ_s , h_s , and T_s , then from (7)

$$T_s - T' = g \frac{r}{2} (\rho' h' - \rho_s h_s) + \frac{1}{6} g r^2 (\rho_s - \rho').$$

Hence, by subtraction

$$T - T_s = g \frac{r}{2} (\rho_s h_s - \rho h) + \frac{1}{6} g r^2 (\rho - \rho_s). \quad . \quad . \quad (8)$$

This is the equation which was used to calculate the value given.

It must be remembered that h , h' , and h_s do not represent the immersed depth of the orifice, but the distance from the surface of the liquid to the vertex of the meniscus when the bubble is about to break away.

If h_1 , h_1' , and h_{s1} are the immersed depths of the jets for the given liquids, then we may say to a sufficient degree of accuracy that

$$h = h_1 + r, \quad h' = h_1' + r, \quad \text{and} \quad h_s = h_{s1} + r.$$

Experimental Details.

1. Investigation of the Variation of the Surface-Tension of Water with Temperature.

The beaker C' was well lagged with asbestos and filled with pure distilled water. It was found that this water evaporated sufficiently during the time required to complete a determination to appreciably affect the values for the surface-tension obtained. In order to correct for this evapora-

tion, it was assumed that $\frac{dh'}{dt}$, where h' is the immersed depth of the jet J' and t the time, was constant during any particular

determination. Consequently, the time at which the balance was set was recorded.

Round the beaker C a heating coil was wound, the coil being imbedded in asbestos. The beaker was filled with pure distilled water which had been boiled to remove dissolved air and then cooled by a mixture of ice and calcium chloride until it began to freeze. The pressures in B_1 and B_2 and the pinchcock P having been adjusted, the tap T_2 was opened and the beaker was gradually raised until the bubbles were just unable to break away from the jet J, but escaped from the jet J'. Owing to conduction from the surrounding air, the temperature of the water was slowly rising. This caused each successive bubble formed at the orifice J to approach nearer to completion than the previous one, until after one or two minutes the bubbles formed at the jets J and J' respectively were absolutely identical, showing that the surface-tension of the water in the beaker C was balanced against that of the water in the beaker C'. The temperature of the water in the beaker C still very slowly rising, the balance turned and a bubble escaped from the jet J. Immediately the thermometer θ was read, the tap T_2 closed so that the free surface of the water should not be disturbed, the screw-pins N and N' set, the thermometer θ' read, and the time taken, in the order stated. The cathetometer microscope, which by means of a micrometer attachment was graduated to $1/200$ th of a millimetre, was set on the upper end of the pin N and the micrometer reading estimated to $1/1000$ th of a millimetre. Only the micrometer attachment was used to set the microscope during the whole determination. The pin N' was not again adjusted until the end of the determination.

The water was heated to about 5°C . by means of the heating coil. The balance having again been obtained, the thermometer θ was read, the screw-pin N set, and the necessary readings taken. Observations were taken at intervals of five centigrade degrees up to 90° or 95°C . When readings were taken at temperatures above that of the surroundings, a small current was kept flowing through the heating coil during the observations so that the temperature would continue to rise very slowly and the balance set. Above 50°C . it was necessary only to keep sufficient current flowing to keep the temperature of the water constant at the desired temperature, for the evaporation was then sufficiently rapid to finally set the balance.

It was difficult to take readings above 90°C . because the

evaporation then becomes very rapid, and furthermore the residue of dissolved air is evolved and disturbs the surface.

The final observation having been taken, the microscope was set on the upper end of the pin N' and its reading taken. The pin was readjusted, the time taken, and the microscope again set and its reading taken. In this way $\frac{dh'}{dt}$ was determined.

The water in the beaker C was siphoned off, the beaker removed, and the depth of immersion of the jet J for the last observation measured by means of a cathetometer microscope graduated to read $1/20$ th of a millimetre. (The instrument used to measure the movement of the pins was only constructed to measure distances in the same vertical line.) It can easily be seen that, starting with the lowest temperature, if $x_1, x_2, x_3 \dots x_n$ are the scale readings corresponding to the temperatures $\theta_1, \theta_2, \theta_3 \dots \theta_n$, the depths of immersion of the jet J for these temperatures are given by

$$(h_1 - x_n) + x_1 \text{ for temperature } \theta_1,$$

$$(h_1 - x_n) + x_2 \text{ for temperature } \theta_2,$$

etc.

etc.

$$h_1 \text{ for temperature } \theta_n,$$

θ_n being the highest temperature recorded and h_1 the depth of immersion corresponding to this temperature.

It was found impossible to keep the temperature θ' of the liquid in the beaker C' constant. The temperature θ was corrected accordingly. It was assumed that θ (corrected) $= \theta + (\bar{\theta}' - \theta')$, where $\bar{\theta}'$ is the mean of the temperatures θ' . This would be accurately true if the relation between the surface-tension and temperature was linear. It is approximately so, and for the purposes of a correction may be regarded as so.

2. Investigation of the Dependence of the Surface-Tension of Solutions of Sodium Chloride on their Concentration.

The beakers C and C' were filled with distilled water. The height of the beaker C was adjusted by means of the screw S until bubbles escaped approximately alternately from the two jets. The pins N and N' were set on the surface of the liquid in the beakers C and C' respectively, the time was taken, and the thermometers were read. The cathetometer microscope was set on the pin N, and its reading taken. Without in any way disturbing the jet J, the water was siphoned from the beaker C, and the latter was removed

and replaced by a clean dry beaker. This was filled with a solution of sodium chloride, the balance again obtained, the pin N set, and the previous readings repeated. Observations were taken for solutions of all concentrations from $12\frac{1}{2}$ to 300 grams per litre. The results were corrected for the evaporation and variation of the temperature of the liquid in the beaker C' in the manner described in the previous section.

If, the balance having been set, a bubble, after breaking away from the jet, did not burst but remained on the surface of the liquid, the consequent extremely slight rise in the level of the free surface of the liquid was sufficient to prevent subsequent bubbles from escaping from that jet.

RESULTS.

$g = 981.2$ dynes per centimetre per centimetre.

Mean radius of the orifice = 0.06059 centimetre.

Substituting these values in equation (8), we obtain the relation

$$T - T_s = 29.73(\rho_s h_s - \rho h) + 0.60(\rho - \rho_s),$$

where h and h_s are measured in centimetres, ρ and ρ_s in grams per cubic centimetre, and T and T_s in dynes per centimetre.

The following table gives some of the values obtained for the surface-tension of water at 15° C. by different observers:—

TABLE I.

T_{15° Dynes per cm.	Observer.	Method.
73.26	Volkmann.	Capillary-rise.
73.46	Domké.	
73.38	Richards & Coombs.	
73.55	Brown & Harkins.	
73.45	Ferguson.	Pull on sphere.
73.45	Hall.	Weighing tension in film.
73.76	Sentis.	Capillary tubes.
73.88	Ferguson.	Jaeger's method.
73.72	Dorsey.	Ripples.
74.22	Watson.	
74.22	Kabähne.	Rippled surface used as diffraction grating.
74.30	Perderson.	Waves on jet.
72.78	Bohr.	

The mean of these values, viz. 73.65 dynes per centimetre, was taken as the surface-tension of water at 15° C. in the following results :—

The Variation of the Surface-Tension of Water with Temperature.

A comparison of the results for four sets of observations of the surface-tension of water from the freezing-point to the boiling-point is given in Table III. The second set of observations is given fully in Table II.

The "correction for h " is that necessitated by the evaporation of the water in the beaker C' during the course of the experiment. It was assumed that h'' , the value of h' at the time of the latter setting of the screw-pin N', was that operative during the complete set of observations, and, in order to justify this assumption, the observed values of h were corrected accordingly. Let t_1 be the time at which a certain observation was taken, and t_2 the time of the latter setting of the screw-pin N'.

Then

$$h'' = h' - \frac{dh'}{dt} (t_2 - t_1),$$

where $\frac{dh'}{dt}$ is the rate of decrease of h' with time. That is, we are assuming the depth of immersion of the jet J' to be $\frac{dh'}{dt} (t_2 - t_1)$ smaller than it actually is. We must therefore assume that the depth of immersion of the jet J is an equivalent amount smaller than it actually is.

Let

$$h_c = h - k(t_2 - t_1), \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where h_c is the corrected value of h .

To a first approximation from equation (7)

$$T - T' = g \frac{r}{2} (\rho' h' - \rho h), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\begin{aligned} T - T' &= g \frac{r}{2} \left[\rho' \left\{ h'' + \frac{dh'}{dt} (t_2 - t_1) \right\} - \rho \{ h_c + k(t_2 - t_1) \} \right] \\ &= g \frac{r}{2} \left[(\rho' h'' - \rho h_c) + (t_2 - t_1) \left(\rho' \frac{dh}{dt} - \rho k \right) \right]. \end{aligned}$$

It is desired to replace equation (10) by the equation

$$T - T' = g \frac{r}{2} (\rho' h'' - \rho h_c). \quad (11)$$

In order that we may do this,

$$\left(\rho' \cdot \frac{dh'}{dt} - \rho k \right) \text{ must be equal to zero.}$$

Therefore

$$k = \frac{\rho'}{\rho} \cdot \frac{dh'}{dt}.$$

Now $\rho = 1.00$ and ρ' lies between 1.00 and 0.96. In order to apply a small correction we may assume that $\rho' = \rho$.

Therefore

$$k = \frac{dh'}{dt}.$$

Equation (9) then becomes

$$h_c = h - \frac{dh'}{dt} (t_2 - t_1),$$

where

$$\frac{dh'}{dt} = \frac{h' - h''}{t_2 - t_1}.$$

If t_1 and t_2 are the times of the former and latter settings of the screw-pin N' respectively, then $h' - h''$ is the difference between the cathetometer microscope readings for these two settings. In this case, t_1 , t_2 , and $(h' - h'')$ being known, a linear graph was drawn from which $(h - h_c)$ for each observation was read off. In this way "h corrected" was obtained.

Equation (7) now becomes

$$T - T' = g \frac{r}{2} (\rho' h'' - \rho h_c) + \frac{1}{6} g r^2 (\rho - \rho'),$$

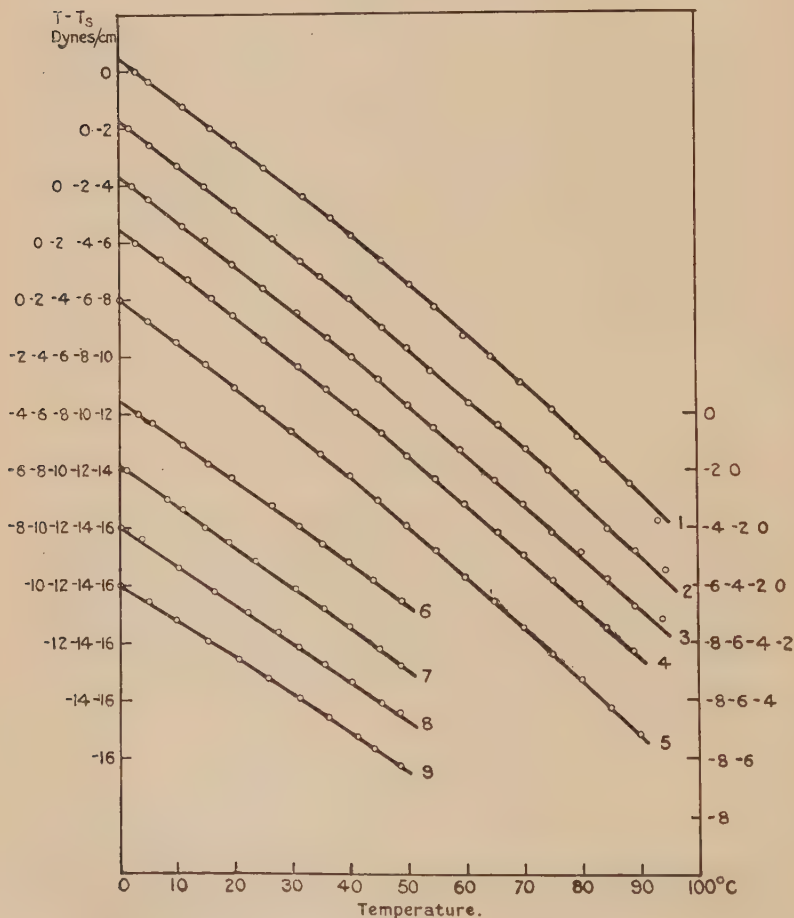
and equation (8) therefore remains unaltered, except that h and h_s must be interpreted as the "corrected" values instead of the observed values. In assuming that $\rho' = \rho$ we have introduced an error of less than 1/100th per cent.

The values of ρ and h corresponding to the first observation were adopted as the standard values, ρ_s , h_s respectively.

The last column, which represents the differences between the surface-tensions at the first temperature corrected and the subsequent temperature corrected, was plotted against the temperature corrected for each set of observations, and the

curves 1 to 4 were obtained (see fig. 6). It can be seen from these curves that $\frac{d^2T}{d\theta^2}$ is comparatively small, and over ranges 0° to 20° C., 20° to 40° C., 40° to 60° C., 60° to 80° C.,

Fig. 6.



and 80° to 90° C. it may be taken as zero, and a linear law may be assumed without introducing any appreciable error ;

$$i. e., \quad T_{\theta_1} = T_{\theta_2} - \frac{dT}{d\theta} (\theta_1 - \theta_2), \quad (12)$$

where $\frac{dT}{d\theta}$ is the rate of decrease of surface-tension with

temperature, and T_{θ_1} and T_{θ_2} are the surface-tensions at the temperatures θ_1 and θ_2 respectively, θ_1 and θ_2 both lying within one of the ranges mentioned. A linear law must not be assumed over any range of 20 centigrade degrees chosen at random, for $\frac{d^2T}{d\theta^2}$ at approximately 40° C. and probably 80° C. is considerable compared with its value in any of the above ranges. More convincing evidence of this fact will be obtained after further analysis of the results.

The figures shown in the columns headed I., II., III., and IV. in Table III. are those derived from the sets of observations I., II., III., and IV. respectively.

Using equation (12), the figures given in the last columns of the four tables of which Table II. is one were corrected to the values they would have had if observations had been taken at temperatures of exactly 0, 5, 10 . . . 90° C. The corrected sets of values are shown in the columns headed "S" of Table III. The deviations of each of the four values of S for each temperature from their mean are shown in the columns headed ΔS . So far we have assumed that no errors were made in the first observation of each set; but this is just as likely to involve errors as any other in that set.

Now the sum of the errors from 0° to 80° C. for each set of observations should be equal to zero (the readings above 80° C. being less consistent than those between 0° and 80 C. were ignored).

Let $a_0, a_5, a_{10}, \dots a_{80}$ be the true values of the errors for any one set of observations corresponding to the temperatures 0°, 5°, 10° . . . 80° C.

Then $\Sigma a = 0$.

Now $(\Delta S)_0 = a_0 - a_0,$

$(\Delta S)_5 = a_5 - a_0,$

$(\Delta S)_{10} = a_{10} - a_0,$

.

.

$(\Delta S)_{80} = a_{80} - a_0.$

Therefore $\Sigma(\Delta S) = -na_0,$

where n is the number of observations between 0° and 80° C.,

or $a_0 = \frac{-\Sigma(\Delta S)}{n} = \frac{-\Sigma(\Delta S)}{17}.$

a_0 for each set of observations was calculated, and the true error for each observation was then determined from the relation

$$a_0 = (\Delta S)_\theta + a_0.$$

The mean error is 0.03 dyne per cm. The mean values of S plotted against temperature are shown in curve 5 (see fig. 6). They can be represented approximately by a second degree equation, viz.

$$S = (0.022 + 0.14618\theta + 0.000241\theta^2) \text{ dynes per cm. (13)}$$

The values of S derived from this equation are shown in the column headed " S calculated." It can be seen from the succeeding column that this equation represents the values of S derived directly from the experimental data to 0.04 dyne per centimetre, which is sufficiently accurate for most practical purposes.

On plotting (S observed — S calculated) against the temperature, a well-defined curve was obtained. The values of (S observed + S calculated) obtained from this curve are shown in the column headed " $(S \text{ obs.} - S \text{ calc.})$ corrected." The differences between the sets of figures in these two columns are irregular, and are therefore probably due to errors of measurement made in the course of the experiments. These "experimental errors" were subtracted from the corresponding S observed in order to obtain " S corrected." The surface-tension of water at 15° C. being known, the surface-tension at each of the other temperatures was calculated.

From equation (13) we may state

$$T_\theta = 75.90(1 - 0.001924\theta - 0.00000362\theta^2) \\ \pm 0.04 \text{ dynes per cm.}$$

The variation of the surface-tension of water with temperature cannot be represented accurately by any equation of the form

$$T_\theta = T_0(1 + a\theta + b\theta^2 + c\theta^3 + \dots).$$

The mean "experimental error" involved in the observed values of S is 0.005 dyne per centimetre. Furthermore, these errors have been eliminated. The values of the surface-tension given in the last column of Table III. are therefore consistent to two decimal places; *i. e.*, to 0.005 dyne per centimetre, or less than 1/100th per cent.

TABLE II. (see Curve 2).
 h' at 2.21 p.m., $-h'$ at 4.28 p.m. = 0.0282 cm. Last $h = 2.755$ cm.

Time.	θ' .	θ .	θ corrected.	x .	h .	Correction for h .	h corrected.	ρ .	ρh .	$\rho h - \rho h_s$.	29.73 ($\rho h - \rho h_s$).	0.60 ($\rho_s - \rho$).	$T_g - T$.
p.m.													
2.21	19.3	1.5	1.7	0.2390	2.1567	0.0282	2.1285	0.9959	2.1283	0	0	0.00	0
2.30	19.25	5.2	5.45	0.2565	2.1742	0.0263	2.1479	1.0000	2.1479	0.0196	0.58	0.00	0.58
2.36	19.25	10.0	10.25	0.2802	2.1979	0.0249	2.1730	0.9997	2.1723	0.0410	1.31	0.00	1.31
2.42	19.25	14.9	15.15	0.3058	2.2235	0.0236	2.1999	0.9991	2.1979	0.0696	2.07	0.00	2.07
2.47	19.2	19.9	20.2	0.3348	2.2525	0.0225	2.2300	0.9983	2.2262	0.0979	2.91	0.00	2.91
2.56	19.25	26.5	26.75	0.3690	2.2867	0.0205	2.2662	0.9697	2.2587	0.1304	3.88	0.00	3.88
3.2	19.3	31.55	31.75	0.3975	2.3152	0.0192	2.2960	0.9952	2.2850	0.1567	4.66	0.00	4.66
3.9	19.3	34.85	35.05	0.4170	2.3347	0.0177	2.3170	0.9941	2.3033	0.1750	5.20	0.00	5.20
3.15	19.35	39.8	39.95	0.4458	2.3635	0.0163	2.3472	0.9923	2.3291	0.2008	5.97	0.00	5.97
3.29	19.4	45.75	45.85	0.4845	2.4022	0.0152	2.3870	0.9899	2.3629	0.2346	6.97	0.01	6.98
3.40	19.45	50.05	50.1	0.5113	2.4290	0.0132	2.4158	0.9880	2.3868	0.2585	7.69	0.01	7.70
3.45	19.55	54.4	54.35	0.5415	2.4592	0.0107	2.4485	0.9860	2.4142	0.2859	8.50	0.01	8.51
3.50	19.6	61.05	60.95	0.5870	2.5047	0.0096	2.4951	0.9827	2.4519	0.3236	9.62	0.01	9.63
3.55	19.65	65.8	65.65	0.6190	2.5367	0.0084	2.5283	0.9802	2.4782	0.3499	10.40	0.01	10.41
3.55	19.7	70.8	70.6	0.6542	2.5719	0.0073	2.5646	0.9773	2.5064	0.3781	11.24	0.01	11.25
3.59	19.8	74.85	74.55	0.6853	2.6030	0.0065	2.5965	0.9750	2.5316	0.4033	11.99	0.02	12.01
4.4	19.85	79.5	79.15	0.7198	2.6375	0.0053	2.6322	0.9721	2.5588	0.4305	12.89	0.02	12.82
4.7	19.9	85.0	84.6	0.7701	2.6884	0.0047	2.6837	0.9686	2.5994	0.4711	14.01	0.02	14.03
4.12	19.95	89.8	89.35	0.8053	2.7230	0.0035	2.7195	0.9655	2.6257	0.4974	14.79	0.02	14.81
4.17	20.1	95.1	94.5	0.8373	2.7550	0.0024	2.7526	0.9619	2.6477	0.5194	15.44	0.02	15.46

Mean = 19.5

TABLE III.

Temp. in °C.	S in dynes per cm.				ΔS.				Experimental errors <i>a</i> .				S calcu- lated.	Sobs.- Scale. cor- rected.	Sobs.- Experi- mental errors <i>b</i> .	S cor- rected.	T.	
	I.	II.	III.	IV.	Mean.	I.	II.	III.	IV.	Numer- ical Mean.								
0	0	0	0	0	0	0	0	0	0	0.05	-0.02	0	0	75.94±0.005				
5	0.73	0.78	0.82	0.65	0.75	-0.02	+0.03	+0.07	-0.10	+0.02	0	-0.03	0	0.75	75.19±			
10	1.52	1.54	1.59	1.43	1.52	0	+0.02	+0.07	-0.09	+0.04	-0.01	0	-0.03	0.02	+0.01	1.51	74.43	
15	2.28	2.32	2.30	2.21	2.28	0	+0.04	+0.02	-0.07	+0.04	+0.01	-0.05	-0.01	0.03	+0.01	+0.02	2.29	73.65
20	3.03	3.15	3.13	3.01	3.08	-0.05	+0.07	+0.05	-0.07	-0.01	+0.04	-0.02	-0.01	0.02	+0.04	+0.04	3.08	72.86
25	3.80	3.88	3.92	3.82	3.85	-0.05	+0.03	+0.07	-0.03	-0.01	0	0	+0.03	0.01	+0.02	0	3.85	72.09
30	4.51	4.66	4.68	4.60	4.61	-0.10	+0.05	+0.07	-0.01	-0.06	+0.02	0	+0.05	0.03	-0.01	-0.01	4.61	71.33
35	5.32	5.46	5.49	5.40	5.42	-0.11	+0.04	+0.07	-0.02	-0.06	+0.01	0	+0.04	0.03	-0.01	-0.03	5.40	70.54
40	6.14	6.25	6.28	6.18	6.21	-0.07	+0.04	+0.07	-0.03	-0.03	+0.01	0	+0.03	0.02	-0.04	0	6.21	69.73
45	6.98	7.10	7.14	7.01	7.06	-0.08	+0.04	+0.08	-0.05	-0.04	+0.01	+0.01	+0.01	0.02	-0.03	-0.03	7.06	68.88
50	7.83	7.95	8.03	7.88	7.92	-0.09	+0.03	+0.11	-0.04	-0.05	0	+0.04	+0.02	0.03	-0.01	-0.01	7.92	68.02
55	8.70	8.89	8.88	8.73	8.80	-0.10	-0.09	+0.08	-0.07	-0.06	+0.06	+0.01	-0.01	0.03	+0.01	+0.01	8.80	67.14
60	9.72	9.73	9.74	9.62	9.70	+0.02	+0.03	+0.04	-0.08	+0.06	0	-0.03	-0.02	0.03	+0.04	+0.04	9.70	66.24
65	10.52	10.56	10.65	10.46	10.55	-0.03	+0.01	+0.10	-0.09	+0.01	-0.02	+0.03	-0.03	0.02	+0.01	+0.01	10.55	65.39
70	11.43	11.41	11.53	11.34	11.43	0	-0.02	+0.10	-0.09	+0.04	-0.05	+0.03	-0.03	0.04	0	0	11.43	64.51
75	12.25	12.36	12.50	12.21	12.33	-0.04	+0.03	+0.17	-0.12	-0.04	0	+0.10	-0.06	0.05	-0.01	-0.01	12.33	63.61
80	13.35	13.24	13.26	13.15	13.25	+0.10	-0.01	+0.01	-0.10	+0.14	-0.04	-0.03	-0.04	0.07	-0.01	-0.01	13.25	62.69
85	14.27	14.37	14.19	14.05	14.22	+0.05	+0.15	-0.03	-0.17	+0.09	+0.12	-0.10	-0.11	0.11	+0.03	0	14.19	61.75
90	15.22	15.20	15.21	14.86	15.12	+0.10	+0.08	+0.09	-0.26	+0.14	+0.05	+0.02	-0.20	0.13	-0.01	+0.01	15.14	60.80
Algebraic Mean						-0.04	+0.03	+0.07	-0.06	Numerical Mean				Numerical Mean...				0.005

The mean value of $\frac{dT}{d\theta}$ obtained from Table III. :

from 0° to 20° C. = 0.154 dynes per centimetre per centigrade degree

„ 20° „ 40° C. = 0.157 „ „ „ „

„ 40° „ 60° C. = 0.174 „ „ „ „

„ 60° „ 80° C. = 0.178 „ „ „ „

„ 80° „ 90° C. = 0.189 „ „ „ „

Therefore, over the ranges 0° to 40° C., and 40° to 80° C., $\frac{d^2T}{d\theta^2}$ is small, and a linear law may be assumed without introducing any error greater than 0.02 dyne/cm.; but at approximately 40° C. $\frac{d^2T}{d\theta^2}$ is considerable, and over a range of any extent including this temperature a linear law must not, on any account, be assumed.

Variation of the Surface-Tension of Aqueous Solutions of Sodium Chloride with Temperature.

The results of four sets of observations with four solutions of different concentrations are shown in Tables IV. to VII.

The experimental procedure and method of calculation was precisely the same as that adopted in the investigation of the variation of the surface-tension of water with temperature. Owing to the rapidity of evaporation, and the consequent increase in concentration, as the temperature increased, it was not considered advisable to take readings above 50° C.

The densities are those obtained by Karsten (Berlin, 1846). Curves 6 to 9 represent the decrease of surface-tension, $T_s - T$, with temperature for the results recorded in Tables IV. to VII. respectively. These curves can be represented to a considerable degree of accuracy from 0° to 40° C. by linear equations, viz.

Solution of 9.38 grams Sodium Chloride per 100 grams solution.

Surface-Tension $T = 78.63 - 0.1416$ dyne/cm.

Solution of 13.66 grams Sodium Chloride for 100 grams solution.

Surface-Tension $T = 80.19 - 0.1404$ dyne/cm.

Solution of 20.76 grams Sodium Chloride per 100 grams solution.

Surface-Tension $T = 83.00 - 0.1329$ dyne/cm.

Solution of 25.17 grams Sodium Chloride per 100 grams solution.

Surface-Tension $T = 85.00 - 0.1265$ dyne/cm.

The absolute values of the surface-tensions at 0° C. were derived from Table IX.

TABLE IV. (see Curve 6).

Solution of 9.38 grams Sodium Chloride per 100 grams solution (100 grams per litre at 20.7° C.).
 h' at 11.14 A.M. — h' at 12.36 P.M. = 0.0170 cm. Last $h = 2.545$ cm.

Time.	θ'	θ .	θ corrected.	α .	h .	Correction for h .	h corrected.	ρ .	ρh .	$\rho h - \rho_s h_s$.	$29.73 \times$ $(\rho h - \rho_s h_s)$.	$0.60 \times$ $(\rho_s - \rho)$.	$T_s - T$.
A.M.													
11.14	18.4	3.25	3.35	0.7675	2.3115	0.0170	2.2945	1.0715	2.4586	0	0	0	0
11.20	18.4	5.6	5.7	0.7772	2.3212	0.0157	2.3055	1.0708	2.4687	0.0101	0.30	0	0.30
11.25	18.4	10.85	10.95	0.8044	2.3484	0.0147	2.3337	1.0693	2.4954	0.0368	1.09	0	1.09
11.30	18.4	15.45	15.55	0.8246	2.3686	0.0117	2.3569	1.0678	2.5167	0.0581	1.73	0	1.73
11.50	18.45	19.45	19.5	0.8430	2.3870	0.0095	2.3775	1.0663	2.5351	0.0765	2.27	0	2.27
12.0	18.5	23.65	23.65	0.8781	2.4221	0.0074	2.4147	1.0635	2.5680	0.1094	3.25	0	3.25
P.M.													
12.4	18.5	31.25	31.25	0.9030	2.4470	0.0066	2.4404	1.0617	2.5910	0.1324	3.94	0.01	3.95
12.9	18.5	35.3	35.3	0.9250	2.4690	0.0055	2.4635	1.0598	2.6108	0.1522	4.52	0.01	4.53
12.14	18.6	40.0	39.9	0.9497	2.4937	0.0045	2.4892	1.0577	2.6328	0.1742	5.18	0.01	5.19
12.19	18.6	44.1	44.0	0.9735	2.5175	0.0035	2.5140	1.0556	2.6538	0.1952	5.80	0.01	5.81
12.24	18.65	49.0	48.85	1.0010	2.5450	0.0024	2.5426	1.0535	2.6786	0.2200	6.54	0.01	6.55

Mean = 18.5

TABLE V. (see Curve 7).

Solution of 13.66 grams Sodium Chloride per 100 grams solution (150 grams per litre at 19° C.).
 h' at 1.49 P.M. $-h'$ at 3.24 P.M. $= 0.0133$ cm. Last $h = 2.12$ cm.

Time.	θ' .	θ .	θ corrected.	x .	h .	Correction for h .	h corrected.	ρ .	ρh .	$\rho h - \rho_s h_s$.	$29.73 \times$ $(\rho h - \rho_s h_s)$.	$0.60 \times$ $(\rho_s - \rho)$.	$T_s - T$.
P.M.													
1.49	18.45	0.8	1.25	0.5536	1.8843	0.0133	1.8710	1.1053	2.0680	0	0	0	0
2.8	18.6	7.95	8.25	0.5855	1.9162	0.0106	1.9056	1.1029	2.1017	0.0337	1.00	0	1.00
2.14	18.7	10.8	11.0	0.5980	1.9287	0.0098	1.9189	1.1018	2.1142	0.0462	1.37	0	1.37
2.21	18.75	14.75	14.9	0.6175	1.9462	0.0088	1.9394	1.1005	2.1343	0.0663	1.97	0	1.97
2.27	18.8	18.9	19.0	0.6362	1.9669	0.0081	1.9588	1.0986	2.1579	0.0839	2.49	0	2.49
2.38	18.9	23.6	23.6	0.6585	1.9892	0.0064	1.9828	1.0965	2.1741	0.1061	3.15	0.01	3.16
2.46	19.0	30.7	30.6	0.6930	2.0237	0.0053	2.0184	1.0931	2.2063	0.1383	4.11	0.01	4.12
2.51	19.0	35.6	35.5	0.7176	2.0483	0.0046	2.0437	1.0908	2.2293	0.1613	4.79	0.01	4.80
2.56	19.1	40.2	40.0	0.7411	2.0718	0.0038	2.0680	1.0887	2.2514	0.1834	5.45	0.01	5.46
3.3	19.15	45.3	45.05	0.7681	2.0988	0.0029	2.0959	1.0861	2.2764	0.2084	6.19	0.01	6.20
3.8	19.25	49.1	48.75	0.7893	0.1200	0.0022	2.1178	1.0842	2.2961	0.2281	6.78	0.01	6.79

Mean = 18.9

TABLE VI. (see Curve 8).

Solution of 20.76 grams Sodium Chloride per 100 grams solution (240 grams per litre at 15°C.).
 h' at 11.25 A.M. — h' at 12.51 P.M. = 0.0073 cm. Last $h = 2.115$ cm.

Time.	θ' .	θ .	θ , corrected.	x .	h .	Correction for h .	h corrected.	ρ .	$r \cdot h$.	$\rho h - \rho_s h$.	$29.73 \times$ $(\rho h - \rho_s h_s)$.	$0.60 \times$ $(\rho_s - \rho)$.	$T_s - T$.
A.M.													
11.25	15.5	-0.4	-0.25	0.2309	1.8919	0.0081	1.8838	1.1626	2.1901	0	0	0	0
11.31	15.5	3.5	3.65	0.2441	1.9051	0.0067	1.8984	1.1610	2.2040	0.0139	0.41	0	0.41
11.41	15.5	10.05	10.2	0.2765	1.9375	0.0058	1.9317	1.1581	2.2371	0.0470	1.40	0	1.40
11.55	15.55	16.45	16.55	0.3040	1.9650	0.0047	1.9603	1.1551	2.2643	0.0742	2.21	0	2.21
P.M.													
12.2	15.6	22.25	22.3	0.3300	1.9910	0.0041	1.9869	1.1523	2.2895	0.0894	2.95	0.01	2.96
12.8	15.65	27.55	27.55	0.3550	2.0140	0.0036	2.0104	1.1498	2.3116	0.1215	3.61	0.01	3.62
12.18	15.7	31.2	31.15	0.3705	2.0315	0.0027	2.0288	1.1480	2.3291	0.1390	4.13	0.01	4.14
12.24	15.75	35.8	35.7	0.3920	2.0530	0.0022	2.0508	1.1455	2.3492	0.1591	4.73	0.01	4.74
12.29	15.8	40.5	40.35	0.4150	2.0760	0.0018	2.0742	1.1428	2.3704	0.1803	5.36	0.01	5.37
12.34	15.8	45.6	45.45	0.4396	2.1006	0.0013	2.0993	1.1400	2.3932	0.2031	6.04	0.01	6.05
12.43	15.9	48.8	48.55	0.4540	2.1150	0.0006	2.1144	1.1383	2.4068	0.2167	6.44	0.01	6.45

Mean = 15.65

TABLE VII. (see Curve 9).
 Solution of 25.17 grams Sodium Chloride=per 100 grams solution (300 grams per litre at 15° C.).
 h' at 1.41 P.M. — h' at 3.19 P.M. = 0.0124 cm. Last $h = 2.025$ cm.

Time.	θ .	θ .	θ corrected.	x .	h .	Correction for h .	h corrected.	ρ .	th .	$h - \rho_s h_s$.	$29.73 \times$ $(th - \rho_s h_s)$.	$0.60 \times$ $(\rho_s - \rho)$.	$T_s - T$.
P.M.													
1.41	14.75	-0.35	-0.2	0.4161	1.8186	0.0124	1.8062	1.1988	2.1653	0	0	0	0
1.59	14.8	4.85	4.95	0.4335	1.8360	0.0102	1.8258	1.1964	2.1844	0.0191	0.57	0	0.57
2.9	14.8	9.6	9.7	0.4530	1.8555	0.0089	1.8466	1.1943	2.2054	0.0401	1.19	0	1.19
2.25	14.9	15.4	15.4	0.4756	1.8781	0.0068	1.8713	1.1916	2.2298	0.0645	1.92	0	1.92
2.30	14.9	20.6	20.6	0.4965	1.8990	0.0062	1.8928	1.1890	2.2505	0.0852	2.53	0.01	2.54
2.39	14.9	25.7	25.7	0.5180	1.9205	0.0050	1.9155	1.1863	2.2724	0.1071	3.18	0.01	3.19
2.45	14.95	31.45	31.4	0.5425	1.9450	0.0043	1.9407	1.1832	2.2962	0.1309	3.89	0.01	3.90
2.53	15	36.35	36.25	0.5646	1.9761	0.0032	1.9639	1.1805	2.3184	0.1531	4.55	0.01	4.56
3.1	15	41.4	41.3	0.5885	1.9910	0.0022	1.9888	1.1778	2.3424	0.1771	5.26	0.01	5.27
3.5	15.05	44.3	44.15	0.6021	2.0046	0.0017	2.0029	1.1761	2.3556	0.1903	5.66	0.01	5.67
3.10	15.05	48.9	48.75	0.6225	2.0250	0.0010	2.0240	1.1734	2.3750	0.2097	6.23	0.01	6.24

Mean = 14.9

TABLE VIII.

h' at 10.33 A.M. — h' at 12.19 P.M. = 0.0176 cm. Last $h = 1.945$ cm.

Concentration, Grams/litre.	Time.	θ' .	θ .	θ cor- rected.	x .	h .	Cor- rection for h .	h cor- rected.	ρ .	ρh .	$(\rho_s h_s - \rho h)$.	$29.75 \times$ $(\rho_s h_s - \rho h)$.	$0.60 \times$ $(\rho - \rho_s)$.	$T - T_s$.	$T - T_s$ corrected to 20° C.
0	10.33	20.4	20.5		1.2740	2.6555	0.0176	2.6379	0.9982	2.6332	0	0	0	0	0
12½	10.44	20.4	20.5		1.2318	2.6133	0.0158	2.5975	1.0063	2.6139	0.0193	0.57	0	0.57	0.57
25	10.55	20.4	20.6		1.1972	2.5787	0.0141	2.5646	1.0156	2.6046	0.0286	0.85	0.01	0.86	0.87
50	11.10	20.4	20.6		1.1305	2.5120	0.0116	2.5004	1.0327	2.5822	0.0510	1.52	0.02	1.54	1.55
100	11.21	20.4	20.7	same as	1.0080	2.3895	0.0098	2.3797	1.0658	2.5363	0.0969	2.88	0.04	2.92	2.94
150	11.35	20.4	20.7	θ .	0.8894	2.2709	0.0074	2.2635	1.0977	2.4846	0.1486	4.42	0.06	4.48	4.50
200	11.46	20.4	20.8		0.7774	2.1589	0.0056	2.1533	1.1288	2.4306	0.2026	6.02	0.08	6.10	6.13
240	11.59	20.4	20.8		0.6885	2.0700	0.0033	2.0667	1.1533	2.3835	0.2497	7.42	0.09	7.51	7.54
300	12.9	20.4	20.9		0.5635	1.9450	0.0017	1.9433	1.1890	2.3106	0.3226	9.59	0.11	9.70	9.73

TABLE IX.

Concentration.		T - T _s at 20° C.				ΔT.			Experimental Errors.				Surface-Tension T at 20° C.
Grams per litre at 20° C.	Grams per 100 grams solution.	X.	XI.	XII.	Mean.	X.	XI.	XII.	X.	XI.	XII.	Arithmetic Mean.	
		0	0	0	0	0	0	0	-0.01	+0.02	-0.01	0.01	72.86
12½	1.24	0.56	0.51	0.57	0.55	+0.01	-0.04	+0.02	0	-0.02	+0.01	0.01	73.41
25	2.46	0.87	0.81	0.87	0.85	+0.02	-0.04	+0.02	+0.01	-0.02	+0.01	0.01	73.71
50	4.84	1.63	1.53	1.55	1.57	+0.06	-0.04	-0.02	+0.05	-0.02	-0.03	0.03	74.43
100	9.38	2.99	2.94	2.94	2.96	+0.03	-0.02	-0.02	+0.02	0	-0.03	0.02	75.82
150	13.66	4.50	4.52	4.50	4.51	-0.01	+0.01	-0.01	-0.02	+0.03	-0.02	0.02	77.37
200	17.71	6.14	6.03	6.13	6.10	+0.04	-0.07	+0.03	+0.03	-0.05	+0.02	0.03	78.96
240	20.80	7.49	7.54	7.54	7.52	-0.03	+0.02	+0.02	-0.04	+0.04	+0.01	0.03	80.38
300	25.21	0.65	9.62	9.73	9.67	-0.02	-0.05	+0.06	-0.03	-0.03	+0.05	0.04	82.53
		Sum = +0.10		-0.23		+0.10		+0.10				Mean = 0.022	
		Mean = +0.01		-0.02		-0.01		+0.01					

Variation of the Surface-Tension of Aqueous Solutions of Sodium Chloride with Concentration.

A comparison of the results of three sets of observations is shown in Table IX. The third set of observations is given fully in Table VIII.

The method of calculation is similar to that adopted in the investigation of the variation of the surface-tension with temperature. It was assumed that the value of θ' during the last observation in each set was that operative during the complete set, and θ was corrected accordingly. If θ'' is the value of θ' during the last observation, then for any subsequent observation

$$\theta \text{ corrected} = \theta + (\theta'' - \theta').$$

The concentration is recorded in grams of Sodium Chloride per litre at 20° C. and also in grams of Sodium Chloride per 100 grams solution. The deviations ΔT of each of the three values of $(T - T_s)$ at 20° C. for each concentration from their mean value are given, and from these the experimental errors were derived. The mean experimental error is 0.022 dyne per cm. The surface-tension of water at 20° C. being known (see Table III.), the surface-tension at the same temperature of each of the solutions could then be derived.

XXXIV. *Electrical Conductivity at Low Temperatures.* By Professor J. C. McLENNAN, F.R.S., and C. D. NIVEN, M.A.*

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5. Summary.

1. *Introduction.*

IT has been known for a long time that the electrical resistance of many pure metals is approximately proportional to the absolute temperature. At low temperatures

* Communicated by the Authors. This work was carried out with the aid of a grant of a bursary and scholarship from the National Research Council of Canada to C. D. Niven.

results have shown that this law is far from true. In the case of some metals the resistance suddenly vanishes altogether before the absolute temperature is reached—a phenomenon called by the late Professor H. K. Onnes superconductivity. In the case of other metals the resistance often tends to a constant value. No satisfactory theory has been advanced for such phenomena, and indeed the data on conductivity at low temperatures are so meagre that any theory would be more or less of a speculation at present. Up till now experimenters have been directing their efforts towards proving or disproving the hypothesis that all metals should be superconducting at very low temperatures. Work by Onnes and his collaborators at Leiden, and Meissner at Charlottenburg indicates that superconductivity is a property of only five metals, namely, mercury, lead, tin, thallium, and indium. In the formulation of any theory on conductivity it is necessary to know the form of the resistance-temperature curves at low temperatures, and an endeavour is being made by the authors of this paper to obtain some data that would be of theoretical value. The results up to the present are communicated in the following paragraphs.

2. Apparatus used in measuring resistances.

Before going into the experimental details of how the different resistances were prepared for measurement, it might be as well to mention how the measurements were made. Readings were taken of the resistances when kept at room temperature, and when immersed in liquid air, liquid hydrogen, and liquid helium. Although at the start of the work measurements were made at the temperature of ice, and carbon dioxide snow dissolved in ether, this procedure was discontinued as there was nothing interesting to be found on the resistance-temperature curves by these measurements. The temperature of liquid air was always taken on a tested pentane thermometer as the variations in temperature depending on how old the air was were sufficient to spoil the continuity of a curve. Temperatures below that of liquid helium were obtained by boiling the liquid helium under reduced pressure, the pressure on the boiling liquid giving the temperature by reference to the vapour-pressure curve.

The measuring apparatus used was so far as possible a Mueller Temperature Bridge which is a particular form of Wheatstone Bridge, and has been fully described by Mueller. The method recommended for eliminating lead resistance on this bridge is by the use of four wires—"potentiometer

leads"—and this method was adopted. Resistances which could quite easily be measured on the bridge at normal temperatures had to be measured on a potentiometer at low temperature. The particular instrument used for this purpose was the Cambridge Instrument Company's Vernier Potentiometer. Comparisons were made with a 0.001 ohm standard resistance and by using large currents very small resistances could be measured.

In order to compare the resistances of the different elements measured, the readings at any particular temperature were multiplied by the specific resistance of the metal at room temperature and divided by the measured value of the resistance at room temperature. As no account was taken in this calculation of the metal contracting, there is an error introduced, theoretically: this error is only about 0.1 per cent. at the most. The specific resistances at room temperature were as far as possible taken from Smithsonian Tables, and where values were not given in the Tables, measurements were made to get them.

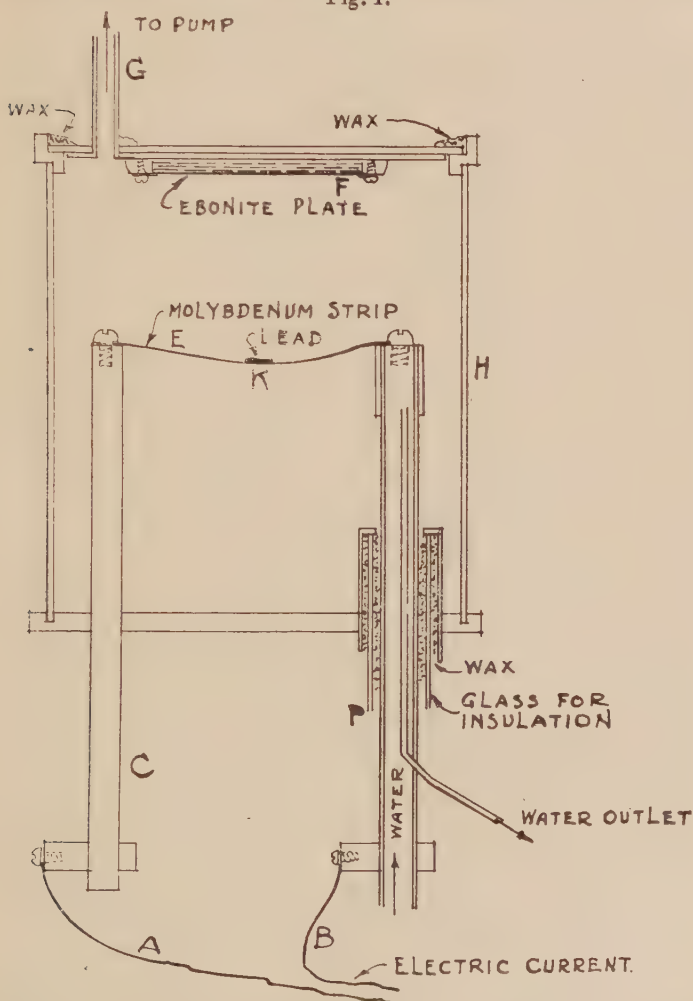
3. *Preliminary work on methods of preparing resistances.*

Before measuring metals which had never been measured before at low temperatures it was considered advisable for a start to take some of the metals which had been investigated by other experimenters and see if we should get the same results as they did. For this preliminary work the elements lead, cadmium, indium, sodium, and potassium were selected, and different methods of making up the resistances exploited.

Method I. used for Lead.—The first metal investigated was lead. Instead of merely taking a wire of lead, it was decided to try and deposit a film on a non-conducting plate, since, if this could be done, it constituted a general method of getting a pure metal in a form that could easily be measured for resistance. In order to make the deposit the small furnace as shown in fig. 1 was employed. The furnace consisted of an evacuated brass vessel through the bottom of which two electrical leads passed; one of these was insulated from the vessel and was therefore watercooled. A molybdenum strip was fixed across the ends of the leads and, when sufficient current was passed through, the molybdenum could be raised to a white heat. In making a deposit the procedure was as follows. The glass or ebonite plate on which the metal was to be deposited was thoroughly cleaned and then clamped to the inside of the

lid of the vessel; a piece of pure lead was placed on the molybdenum strip, the lid was then waxed on to the vessel, and the latter evacuated; when all the oxygen was

Fig. 1.



exhausted the current was put on. Care had to be taken not to put on too heavy a deposit as there was then a tendency for it to peel off; the best deposits were got by passing a current of 35 amperes for about one minute through the particular molybdenum strip in use. Lines

were then carefully drawn up and down the deposit, every alternate line being drawn right through to one end of the plate. In this way a long narrow conducting surface like a zig-zag ribbon was left. In order to provide for contacts, two holes had been bored in the plate before depositing the film and the deposit was left untouched round these holes. The conducting ribbon of deposit terminated at each of these holes. Two comparatively heavy pieces of copper on which the leading-in wires were soldered were then securely clamped on by means of a screw and nut passing through each hole. A spring washer was placed under the nut to allow for contraction in cooling. The first deposits were made on glass, but when these were placed in liquid air the ribbon of lead contracted and broke. It was therefore necessary to get a material other than glass, on which to deposit the film. Such a material had to be an insulator and non-reactive with metals, and it had also to have a coefficient of expansion at any rate as great as the coefficient of expansion of the metal deposited on it. Ebonite seemed to fulfil these requirements, and on being tried proved satisfactory. The resistance of the deposits seemed to alter, growing larger if left over night, and it was concluded that this was due to oxidization; after coating the deposit with collodion this alteration in conductivity ceased. The conductivity of a film of lead deposited on ebonite and thus treated was found to remain unaltered for months even though cooled repeatedly to the temperature of liquid helium and allowed to warm up again.

The resistance of the film thus prepared was found to decrease with temperature according to a linear relation right down as far as the temperature of liquid hydrogen. If the curves in figs. 3 and 4 be looked at it will be observed that had the straight line been continued, the resistance of the lead would have vanished at about 7° K. When the resistance was measured at the temperature of liquid helium, the value was found to be zero. The lead had become superconducting. The question then remained to be answered, did the resistance gradually diminish according to the linear relation or did it suddenly disappear as Professor H. K. Onnes had found for a lead turning? In order to ascertain this, it was decided to try and take readings on a Constantan Resistance Thermometer—which had previously been calibrated in liquid air, liquid hydrogen, and liquid helium—simultaneously with the readings on the lead resistance, while the flask was warming up after having liquid helium in it. The Constantan Resistance Thermometer was read

on the Temperature Bridge, and in the first attempts the lead resistance was measured on the potentiometer. Two difficulties were encountered: in the first place, the potentiometer took too long to read, and in the second place, it seemed as if the temperatures of the two resistances were not really the same. This appeared from the fact that when the flask was warming up after liquefying helium, the constantan resistance reached the temperature of liquid hydrogen before the lead one did. In order to overcome the first difficulty, the potentiometer was abandoned and a very delicate milli-voltmeter substituted. An ammeter was put in series with the lead film resistance. In this way readings would be taken very quickly. The second difficulty was overcome by taking the readings while the flask was being cooled down from liquid hydrogen temperature. The cooling was done very slowly by upsetting the ideal conditions for making liquid helium, for instance, by having the wrong pressure at the expansion nozzle. It was much better to allow the flask to cool down slowly like this for taking the readings than to allow it to heat up slowly by radiation from outside or from the expansion nozzle, as the gas was in circulation all the time and there were therefore no temperature gradients inside the flask to cause the resistances to be at different temperatures. The results obtained were very satisfactory. As the temperature fell the pointer on the millivoltmeter went steadily back until a certain value was reached when suddenly it fell down to zero; by allowing the flask to heat and then by cooling again, this point on the millivoltmeter was crossed several times and the value of the constantan resistance noted each time; the results on the latter resistance always agreed and it corresponded to a temperature of $7^{\circ}5$ K. The late Professor H. K. Onnes found $7^{\circ}2$ K. for the vanishing point of the resistance of the sample of lead turning investigated by him in his special cryostat described in 'Communications from Leiden,' No. 160. The measurements of the lead film are shown in Table I.

Method II. used for Cadmium and Indium.—Another method employed for getting resistances was to roll a rod of the metal into a long strip, then to cut a ribbon of the metal off the side of the strip and wind it on to a glass rod or piece of ebonite. This method was used in the case of cadmium and indium. The method had the disadvantage that only certain metals—namely, those that are malleable—yield to such treatment; and, again, with the large majority of metals, the operation of rolling would so destroy

their crystal structure that their resistance would be altered. It was, therefore, considered necessary to make two resistances of cadmium and "age" one but not the other ; such a precaution was not taken with indium as its melting-point is only 155° C. and the metal rolled very easily.

TABLE I.

CADMIUM—unaged—I.			CADMIUM —aged—I.		
Degrees Kelvin.	Ohms.	Specific Resistance.	Degrees Kelvin.	Ohms.	Specific Resistance.
288	2.703	7.48	293	0.778	7.60
80	0.669	1.81	83	0.192	1.89
20.6	0.068	0.184	20.6	0.0147	0.144
4.2	0.0129	0.035	11.5	15.7×10^{-4}	15.3×10^{-3}
3.8	0.0128	0.035	9.8	9.0	8.8
CADMIUM—aged—II.			9.2	8.5	8.3
Degrees Kelvin.	Ohms.	Specific Resistance.	8.2	6.2	6.1
297	8.71	7.70	4.2	5.2	5.1
81	2.052	1.82	LEAD (film).		
20.6	0.160	0.141	Degrees Kelvin.	Ohms.	Specific Resistance.
4.2	6.2×10^{-3}	5.5×10^{-3}	273	17.93	20.4
3.6	6.1	5.4	82	5.09	5.79
INDIUM.			20.6	0.87	0.99
Degrees Kelvin.	Ohms.	Specific Resistance.	14.4	0.54	0.61
296	0.195	9.10	12.0	0.45	0.51
81	0.046	2.15	10.3	0.40	0.46
20.6	0.012	0.337	7.6	0.35	0.40
4.2	6.9×10^{-3}	0.322	7.5	0.34	0.39
3.38	6.8	0.317	7.4	zero	zero
3.37	zero	zero			

Cadmium.—The strip of cadmium was wound on a piece of pyrex glass; asbestos was used as insulation and the resistance was aged at 200°C . for $3\frac{1}{2}$ hours. The leading-in wires were soldered on. Measurements were made on the aged and on the unaged resistances and the slopes of the curves agreed very well down as far as liquid air, but below that temperature the resistance of the aged cadmium went lower than that of the unaged, until at the temperature of liquid helium the resistance of the unaged was almost seven times that of the aged. There was some doubt at the time that this work was being done as to whether cadmium was superconducting or not, although since then Meissner has definitely shown that it is not. In view of this doubt it was decided to make a much higher resistance and put only a small current through it in measuring the resistance, thus reducing the effect of the magnetic field caused by the flowing current. The resistance was measured in liquid helium with a current of $\cdot 01$ ampere flowing through it, and no diminution of the value was noticed from what it measured with $\cdot 1$ ampere.

By reducing the pressure on the helium the resistance was read down to $3^{\circ}\cdot 6\text{ K}$. but no sign of superconductivity could be observed, and indeed the resistance-temperature curve seemed to be almost parallel to the temperature axis below 8° K . At higher temperatures—between 20° K . and 300° K .—the curve is almost linear and resembles lead in that respect. The residual resistance of cadmium which we obtained agrees well with Meissner's value. By referring to the curve, $\frac{R}{R_0}$ can be calculated and is found equal to

$7\cdot 80 \times 10^{-4}$, while Meissner* gives $7\cdot 60 \times 10^{-4}$ for an "aged" sample of cadmium wire.

Indium.—Although indium did not require to be aged on account of its extreme softness, yet other difficulties in handling it arose. When it was rolled, it spread into such a thin foil that it could hardly be touched without breaking. A ribbon about 2 cm. wide was cut off the edge, laid on a piece of ebonite, and screws passing through four holes in the ebonite at once clamped on four minute copper plates carrying the leads and at the same time held the indium tight against the ebonite. Measurements were made down to the temperature of liquid helium, and then the helium was boiled off under reduced pressure. Improvements had to be made in the pumping system for reducing the pressure

* Meissner, *Zeit. für Phys.* xxxviii. No. 9/10, 1926, p. 647.

before the temperature could be reached at which Professor H. K. Onnes had found indium superconducting, and when these improvements were made we could read temperatures well below 3° K. The pressure at which the resistance of indium vanished was 290 mm. of mercury, which is rather lower than what Professor H. K. Onnes found; this pressure corresponds to a temperature of $3^{\circ}\cdot38$ K. while the pressure given by Onnes corresponds to $3^{\circ}\cdot42$ K. This is a difference of four hundredths of a degree. It is interesting to observe that the resistance-temperature curve for indium is not linear between 20° K. and 300° K. It has a distinct curvature compared with either lead or cadmium, and in this respect resembles the alkali metals.

Method III. used for Sodium and Potassium.—Another method which is practically the same as the one used by Guntz and Bromiewski* was used in the preparation of resistances for metals which, though easily oxidized, yet would distil in vacuo. A fine pyrex glass capillary was drawn out and bent into a U, each arm being about 4 inches long. At either end, the capillary was blown out into a bulb, about 5 mm. in diameter, and into each of these bulbs two tungsten electrodes were sealed. The electrodes projected well into the centre of the bulbs, but did not touch each other. In one of these bulbs a finely drawn-out tube was sealed leading up to a large bulb A, shown in fig. 2. The bulb A was about $2\frac{1}{2}$ cm. in diameter; to this bulb was sealed a tube with a stopcock D and open end E, and also a fine tube leading through a similar bulb B to the bulb C in which the sodium or potassium was placed. The whole apparatus was exhausted by connecting E to a pump, and as soon as a good vacuum was reached the stopcock D was closed and the metal in C was distilled first to B and then to A. The bulbs B and C were then removed. The open end E was then connected to a nitrogen tank with manometer in series; the U-tube and bulb A were immersed in glycerine heated to about 160° C.; the stopcock D was opened, and nitrogen at atmospheric pressure forced the molten metal through the capillary, all oxidation being thus avoided. Finally, the bulb A was fused off.

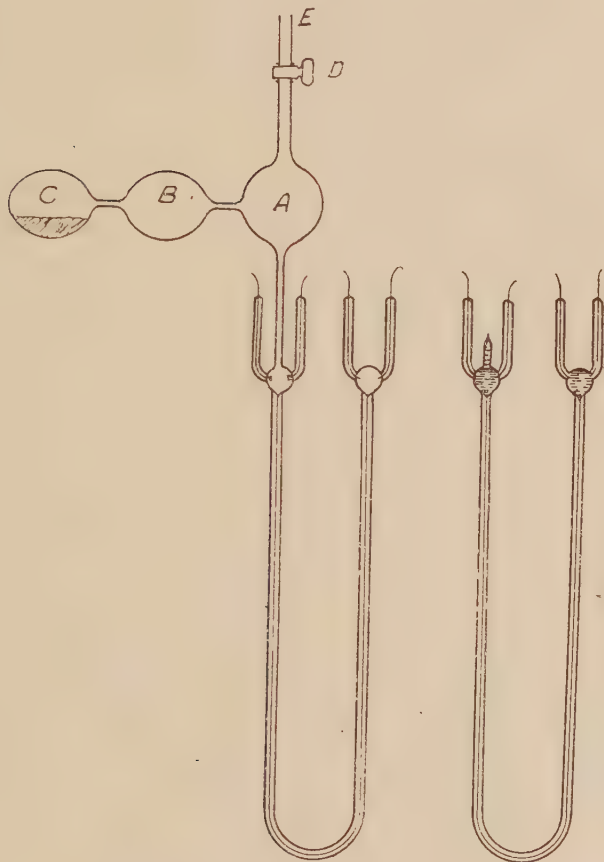
Measurements were made on sodium and potassium down as far as the temperature of liquid hydrogen, and agreed with what other experimenters found.

With regard to the three methods outlined above, it might be remarked that Methods II. and III. are necessarily of

* Guntz and Bromiewski, *Comp. Rend.* 1908, p. 1474.

limited application—one depending on the malleability of the metal and the other on the ability to distil at a low temperature. Method I., which might have been expected to be of more general application, is rather disappointing.

Fig. 2.



Even if the difficulties of the distillation be overcome, the film after it is deposited is liable to be damaged by the contraction of the plate—glass or ebonite—in low temperature work. This trouble was not foreseen when we started making the lead deposit. The results with lead show that the method has possibilities, and when other avenues of attack fail this method might be used.

4. *Investigation of some resistance-temperature curves.*

In addition to repeating the measurements on lead, indium, and cadmium, the resistance-temperature curves of beryllium, chromium, rubidium, thorium, and an alloy of sodium and potassium were investigated. The remainder of this communication will be devoted to describing the work on these metals. The readings for beryllium, chromium, rubidium, and thorium are given in Table II, and those for the sodium-potassium alloy in Table III.

TABLE II.

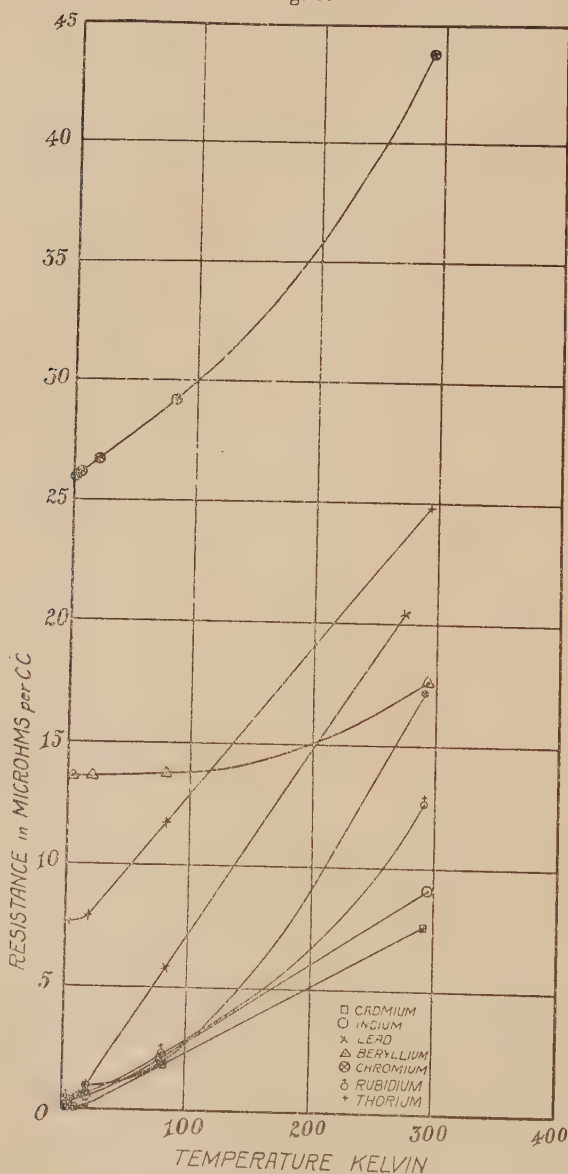
BERYLLIUM.			CHROMIUM—unaged—I.		
Degrees Kelvin.	Ohms.	Specific Resistance.	Degrees Kelvin.	Ohms.	Specific Resistance.
293	8.17×10^{-4}	17.6	290	1.71×10^{-2}	43.8
81	6.39	13.7	83	1.14	29.2
20.6	6.36	13.6	20.6	1.04	26.7
4.2	6.34	13.6	4.2	1.02	26.2
			2.35	1.01	25.9
RUBIDIUM.			CHROMIUM—unaged—II.		
Degrees Kelvin.	Ohms.	Specific Resistance.	Degrees Kelvin.	Ohms.	Specific Resistance.
293	0.735	12.6	290	9.16×10^{-3}	43.8
82	0.134	2.30	83	6.03	28.8
20.6	0.0384	0.658	20.6	5.64	27.0
4.2	0.0208	0.357	4.2	5.58	26.7
2.63	0.0206	0.353	3.01	5.57	26.6
			2.20	5.55	26.5
THORIUM.			CHROMIUM—aged—I.		
Degrees Kelvin.	Ohms.	Specific Resistance.	Degrees Kelvin.	Ohms.	Specific Resistance.
295	1.134	24.83	292	5.59×10^{-3}	17.2
81	0.535	11.72	80	0.655	2.01
20.6	0.357	7.82	20.6	0.260	0.90
4.2	0.348	7.62			
2.93	0.348	7.62			

(i.) *Beryllium*.—The sample of beryllium was obtained from the Beryllium Corporation of America. It would not solder and so clamps had to be used for carrying the terminals. The specific resistance of the sample was taken and found to be 17.6 microhms at 20° C. This indicated that beryllium was a comparatively poor conductor. We also found that its resistance-temperature curve behaved in a rather unexpected manner. Instead of dropping down towards the origin, it remained high, and curved off away from the temperature axis, similar to other metals. The temperature gradient at low temperatures was exceptionally small; in that respect it was comparable with the gradient of cadmium. No sign of superconductivity, when measured in liquid helium under reduced pressure, was detected.

(ii.) *Chromium*.—A sample of chromium was obtained from the General Electric Company of England through the kindness of Mr. C. C. Paterson. This was in the form of a sheet that had been electrolytically deposited. It was very hard and brittle. It was impossible to cut a strip off the side of a sheet with a carborundum saw, owing to the chromium chipping off. Eventually pieces suitable for resistance measurements were obtained by grinding down small pieces of the sheet to strips about $1\frac{1}{2}$ inches long and $\frac{3}{16}$ inch broad. Subsequently strips were successfully obtained by dissolving in acid with the aid of an electrical potential. The sheet chromium was stuck on to a piece of wood with vaseline and painted over the face with vaseline; lines were drawn through the vaseline so as to allow the acid to get into the chromium when the piece of wood was standing in acid. A steel point was made to press against the chromium through the vaseline, and a wire from the positive terminal of the battery led to this point. A second wire from the negative terminal led to a copper plate also standing in the acid. In this way a strip of chromium could be cut off roughly. Its edges could then be ground smooth on a carborundum wheel. In fixing on the leads, solder could not be used as chromium will not solder. The sheet was so brittle that small clamps did not seem desirable. It was decided, therefore, to electroplate small portions at the ends of the chromium strips and then to solder on the leads. The specific resistance measurements were made between steel points.

Chromium presented a problem that appeared to us of great interest. The value given in Smithsonian Tables for the specific resistance of chromium was 2.6 microhms. This indicated that chromium should be an exceptionally good

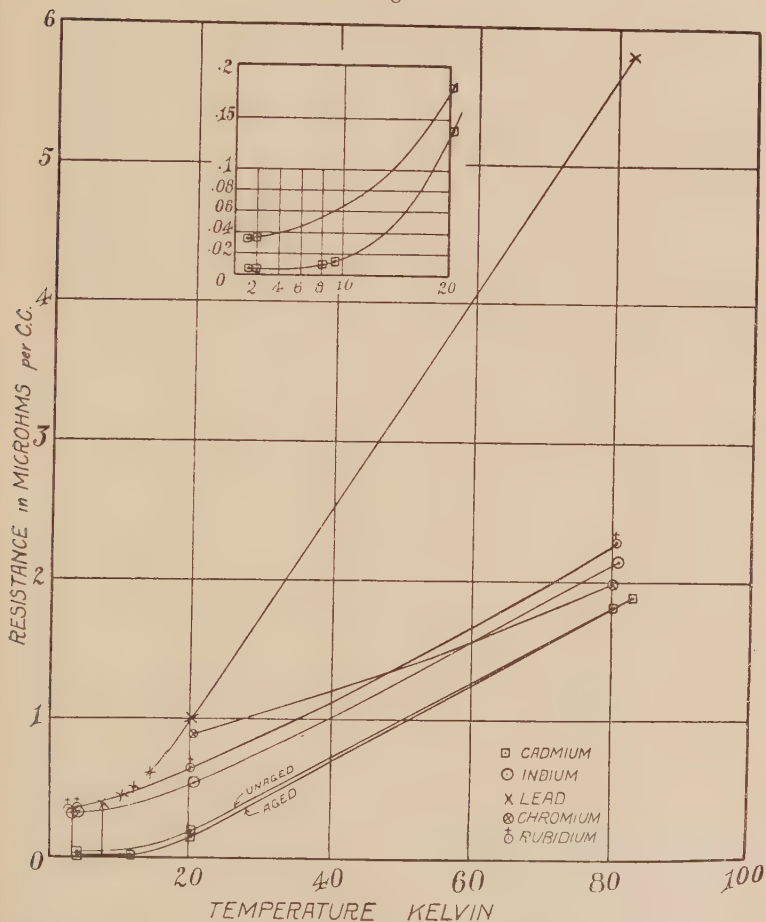
Fig. 3.



conductor, and as recent spectroscopic results showed that chromium should have one electron in the outside system, it appeared as if chromium would behave like an alkali so far as conductivity went. At the start of the work as much

information as possible was collated about this measurement on the specific resistance of chromium. It was done by Shukov, and the abstracts of the original paper (which were in Russian) showed that the work had been done more from a point of view of getting the effect of a nitride of

Fig. 4.



chromium on the resistance. Our value of the specific resistance—which was 44 microhms, and therefore 16 times greater than Shukov's, as a reference to his paper * will show—was possibly due to occluded hydrogen gas in the metal, or to the metal being impure. The metal was tested spectroscopically and found to give only a trace of copper, but the

* *Jurn. Russk. Fizik-Chimicesk. Obscestva*, xlii. pp. 40-41 (1910).

amount was so small that it was not sufficient to account for the high result we obtained. We accordingly decided to heat the chromium to try to drive off the occluded hydrogen gas. This we succeeded in doing.

The furnace in which the chromium was heated consisted of a small quartz tube inside of a coil of nichrome wire. The whole furnace was surrounded by an evacuated glass bulb. The sample was aged for only one hour at the comparatively low temperature thus obtained. It was then taken out and measured for specific resistance at room temperature and also for temperature variation between room temperature and liquid air. The specific resistance was found to be 17.41 microhms and the ratio of the resistance at room temperature to the resistance at liquid air temperature to be 7.3. The strip of chromium was then put back in the furnace and surrounded this time with a tungsten coil and heated for two hours at the much higher temperature thus obtainable. It was taken out and again measured for specific resistance and temperature gradient. This time the specific resistance at room temperature was found to be 17.25 microhms and the ratio of the resistance at room temperature to that at liquid air temperature to be 8.5. The reason for the comparatively high change in the temperature gradient without an appreciable alteration in the specific resistance is not quite understood.

The strip of chromium thus aged was then measured in liquid hydrogen. Unfortunately, owing to trouble with the plant for making the liquid helium, the reading at liquid helium temperature was not obtained; the results down to liquid hydrogen are given, nevertheless, so that the resistance-temperature curves for the aged and unaged strips of chromium may be compared. A glance at the curves shows that to a first approximation the ageing apparently had the effect of moving the whole curve down towards the temperature axis; on closer examination it can be observed that at the temperature of liquid hydrogen the gradient for the aged strip was less than for the unaged. The resistance-temperature curve of chromium has a decided curvature, and in this respect resembles those of the alkali metals and indium; as in the case of other pure metals, the temperature gradient at very low temperatures is small.

(iii.) *Rubidium*.—A U-shaped capillary was filled with the metal exactly as described above in Method III. Although the melting-point of rubidium is 30°C. , which is above room temperature, yet considerable inconvenience was caused by the thread of metal breaking at low temperatures. The readings for rubidium were taken below 3°K. ; there

was no sign of superconductivity. The resistance-temperature curve showed the distinct curvature found in the curves for the other alkali metals, and the usual small temperature gradient at very low temperatures. The value for the specific resistance was taken from Smithsonian Tables.

(iv.) *Thorium*.—The sample of wire obtained through the kindness of D. Ralph E. Myers, of the Westinghouse Lamp Company, when examined would not solder and so pressure-contacts were employed in measuring the temperature gradient. Readings were taken down to 3°K . The resistance-temperature curve almost obeyed a linear relation right down to liquid hydrogen temperature. At lower temperatures it curved round, having almost a zero gradient at liquid helium temperature. No sign of super-conductivity was observed; the specific resistance was $24\cdot83$ microhms at 20°C .; this value as well as the linear form of the resistance-temperature curve pointed to a similarity between lead and thorium.

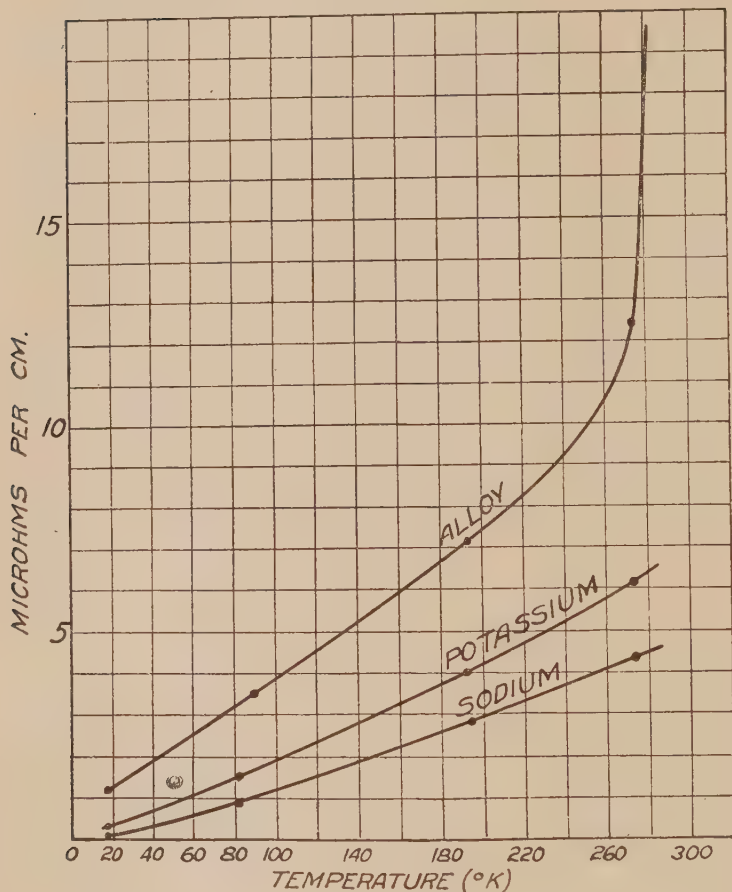
(v.) *Alloy of Sodium and Potassium*.—This work was undertaken to ascertain whether an alloy of sodium and

TABLE III.

SODIUM.			POTASSIUM.		
Degrees Kelvin.	Ohms.	Specific Resistance.	Degrees Kelvin.	Ohms.	Specific Resistance.
273	0.191	4.3	273	0.916	6.1
195	0.127	2.9	191	0.600	4.0
81	0.041	0.91	80	0.240	1.6
20.6	0.004	0.09	20.6	0.045	0.35

ALLOY.		
Degrees Kelvin.	Ohms.	Specific Resistance.
293	3.342	28.6
273	1.481	12.5
192	0.826	7.1
88	0.466	3.6
20.6	0.144	1.2

Fig. 5.



potassium had a resistance curve like that of either of the elements composing it. A U-tube was made as described in Method III. except that it had in addition sealed into the bulb A another distilling-tube to permit sodium as well as potassium to be distilled in, also a small tube to take a little sample of the alloy, and a long capillary to take a measurement of the specific resistance of the alloy. The small sample was used to get the melting-point, which, by reference to the melting-point diagram* for sodium-potassium

* Kurnakow and Puschine, *Zeit. für anorg. Chem.* No. 109, p. 30.

alloys, gave the composition. The results of the experiment are given below. The melting-point of the alloy used indicated an atomic percentage of 55 per cent. potassium and 45 per cent. sodium. This melting-point diagram is of interest in that it suggests that a chemical combination is formed of formula K_2Na .

It can be seen from fig. 5 that the resistance-temperature curve of the alloy obeys a linear relation, very nearly from 20° K. up to its melting-point, while, on the other hand, there is a distinct curvature in the case of the pure metals. A closer study of the curves shows that while at higher temperatures the resistance of the alloy approximates to the sum of the resistances of the pure metals, yet nearer the absolute zero the resistance of the alloy remains high compared with the resistance of either of the pure metals. The observations are in agreement with the theory that at zero degrees absolute the important factor is the phase of the electron in the outermost orbit, while at higher temperatures the thermal agitation eclipses this effect.

5. *Summary.*

1. The resistance-temperature curves of lead, cadmium, and indium were investigated and the results found confirmed the work of other experimenters.

2. Resistance-temperature curves of samples of beryllium, chromium, rubidium, and thorium were investigated. The results showed that the temperature gradient was small for all pure metals at very low temperatures except for those that were superconducting; and even in the case of the latter the temperature gradient rapidly diminished just before the sudden disappearance of the resistance.

3. The results obtained for chromium showed it to be a fairly poor conductor with a steep temperature gradient at room temperature. The effect of ageing electrolytic chromium was to reduce its specific resistance at room temperature from 44 to 17 microhms; the very high value for the electrolytic chromium was due to occluded gas, and when this was driven off the resistance-temperature curve was moved down towards the temperature axis with very little alteration in its shape.

4. The resistance of rubidium was measured at $2^\circ.63$ K, and no sign of superconductivity was apparent.

5. The resistance-temperature curve of an alloy of sodium and potassium was investigated down to the temperature of liquid hydrogen. It resembled the curves for the pure

metals composing it; the curve for the alloy indicated a much higher resistance at 0° K. than the residual resistance of either sodium or potassium.

In conclusion we should like to express our indebtedness to Dr. R. Ruedy and Mr. H. S. Wynne-Edwards for examining the chromium spectroscopically and for ageing it in the furnace they were using. The glass-blowing connected with the preparation of the alkali metal resistances was admirably done by Mr. Chappell, glass-blower to the Physics Department of the University of Toronto.

Professor McLennan wishes to take this opportunity of expressing his appreciation of the financial aid given by the National Research Council of Canada and by the Carnegie Corporation, without which this and other low-temperature investigations could not have been undertaken.

The Physical Laboratory,
University of Toronto.
June 29, 1927.

XXXV. *The Effect of Radon on the Solubility of Lead Uranate.*
By KENNETH C. BAILEY, *Sc.D.*, *Fellow of Trinity College,*
Dublin *.

IN a communication on "Estimates of Geological Time" (Phil. Mag. vol. i. pp. 1055-74, 1926), A. Holmes suggests that the difference existing between the estimates based on the lead-thorium ratio in thorium minerals and those based on the lead-uranium ratio in uranium minerals is due to the fact that, in the latter case, most of the lead produced would probably form lead uranate, which is practically insoluble, while in the former the relatively soluble lead thorate would be formed and partially removed by leaching.

The fact that a compound is insoluble "*in vitro*" does not prove that the same compound will be insoluble when subjected to a radioactive field; and, although the field produced in the case of a uranium mineral is feeble as compared with that available in the laboratory, its action has probably continued over many millions of years—a fact which may well compensate for its lack of intensity. Moreover, such minerals usually contain traces of other compounds,

* Communicated by Prof. J. Joly, D.Sc., F.R.S.

such as chlorides, which might interact with lead uranate under the influence of radiation to form soluble substances.

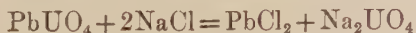
Lead uranate (PbUO_4), whether boiled for some hours with distilled water or left in contact with distilled water for several weeks, remained quite insoluble. The supernatant liquid gave no colour with sodium sulphide, even when evaporated to one-tenth its volume with a few drops of nitric acid, to prevent the deposition of any lead which had gone into solution, and made alkaline before testing. Further, no lead passed into solution when lead uranate was boiled for some hours with a solution of sodium chloride.

Experiments with Radon.

(A) A layer of lead uranate, immersed in a solution of sodium chloride, was subjected to the action of about 160 mcs. of radon until the degradation of the latter to Ra D was approximately complete. The conditions were not very favourable, as the gaseous radon in the upper part of the vessel was separated from the solid lead uranate by a layer of water several cms. thick. α -particles could therefore only reach the lead uranate from the dissolved radon immediately in contact with it.

The solution did not darken on addition of sodium sulphide, but when a portion of it was evaporated to about one-tenth its volume, it gave a dark colour and eventually a slight precipitate with sodium sulphide. A very small amount of lead had evidently been brought into solution.

(B) In order to improve the efficiency of radiation, finely powdered lead uranate was sprinkled over the interior of a glass separating funnel fitted with a ground-glass stopper, and moistened with a strong solution of sodium chloride. The funnel was exhausted, and 120 mcs. of radon admitted and left till degraded to Ra D. The contents were then washed out with distilled water and tested for lead (as before) and for uranium (yellow colour produced by the addition of hydrogen peroxide and sodium hydroxide to the lead-free solution). Both tests were strongly positive, and colorimetric estimation indicated that 0.011 gm. of lead and 0.013 gm. of uranium had gone into solution. The weight of uranium corresponding to 0.011 gm. of lead in the molecule PbUO_4 is 0.0127 gm. This suggests that the reaction



has been promoted by the action of radon, the products on the right-hand side going into solution.

(C) An experiment was performed under similar conditions to (B) in which the lead uranate was moistened with distilled water, no sodium chloride being added. 115 mcs. of radon were employed.

0.0043 gm. of lead went into solution, but no uranium could be detected in solution. The evidence was not sufficient to indicate the form in which the lead became soluble.

(D) In order to determine whether the entire action is due to α -radiation, lead uranate in contact with sodium chloride solution was subjected for about four months to β - and γ -radiation by placing it about an inch from a glass flask containing radium bromide in solution. A trace of lead, detected only after evaporation of the solution to one-fifth its bulk, went into solution. This experiment made it clear that almost, though not quite, all the reaction produced in (B) was due to α -particles.

A blank experiment with the vessel used in A, B, and C showed that no lead is brought into solution by the action of radiation on the glass.

Calculations of the chemical action due to each α -particle were made on the results of (B) and (C). Such calculations can only be approximate, the most uncertain factor being the fraction of the glass surface actually covered in each experiment with lead uranate.

The number of α -particles per 1000 mcs. per second was taken as 3.5×10^{10} , the average life as 5.55 days, and the mass of the atom of hydrogen (from which the mass of the atom of lead was calculated) as 1.66×10^{-24} gm. An error is introduced by the assumption that the entire action is due to α -particles; but the error has been shown to be small.

Assuming that one-quarter of the glass surface was covered in (B) and one-half in (C) (visual estimation), we find that in (B) each α -particle caused the reaction and entry into solution of about 21,300 molecules of lead uranate, while in (C) each α -particle brought into solution about 4300 atoms of lead.

It is clear, as a result of these experiments, that the lead-uranium ratio in a uranium mineral is likely to be considerably affected by the entering into solution of both lead and uranium under the influence of the radioactive field due to the mineral itself. If we assume that a lead uranate is formed and, under the influence of strong ionization, is brought into solution and removed, then equal numbers of atoms of uranium and lead will disappear; and, as this involves a larger percentage-reduction of the lead than of the uranium present, it follows that estimates of geological time based upon

the lead-uranium ratio will err on the side of insufficiency. If the conditions approximate more closely to those of experiment C than to those of experiment B, the percentage-reduction of lead as compared with that of uranium will be still greater.

The foregoing results show that the "*in vitro*" insolubility of lead uranate cannot be regarded as applying to this compound when associated with the parent substances. If there is leaching at all, we must face the probability that removal of lead has taken place, and at a rate fast compared with the rate of its genesis. Again, where age-long time-periods are involved, it seems doubtful if any differential removal of thorium-lead as compared with uranium-lead can be safely assumed, the time-periods required for the removal of lead in both cases being probably insignificant as compared with the period required for its formation.

I desire to express my thanks to Professor Joly, F.R.S., who suggested this subject for research; to Professor E. A. Werner, Sc.D., for the sample of lead uranate employed; and to Dr. H. H. Poole, Chief Scientific Officer of the Royal Dublin Society, for the radon used in these experiments.

University Chemical Laboratory,
Trinity College, Dublin.

XXXVI. *Some New Regularities in Atomic Spectra.* By Professor J. C. McLENNAN, F.R.S., and A. B. McLAY, Ph.D.*

I. Introduction.

INVESTIGATIONS by the authors and others on the arc spectra of many of the elements in each of the five short periods of six, *i. e.* B to Ne, Al to Ar, etc., have shown that the outermost electrons of each neutral atom in its normal state occupy equivalent n_2 orbits, where $n = 2, 3, \dots$ and 6 respectively for the 1st, 2nd, ... and 5th periods. There are respectively one, two, ... six outermost electrons in the atoms of the elements of each of the B, C, ... Ne groups. For the most easily excited of the higher energy states one of the outermost electrons is displaced to an $(n+1)_1$ orbit, the rest remaining in their original n_2 orbits.

The configuration of the outermost electrons of the

* Communicated by the Authors.

neutral atoms under consideration when in the above-mentioned states is given in Table I. in the rows A and B respectively. Together with them the spectral terms are given that should characterize each state. In the table the theoretically deepest term is at the left, and the order of the components of any multiple term is indicated by the order of the term subscripts, the left one representing the deepest component.

TABLE I.

Atomic No.	Atoms.	Electron Configuration.		Terms.
			$n_2, (n+1)_1$	
N*	B, Al Fi	A	1 —	2S_1
		B	— 1	$^2P_{12}$
N+1	C, Si Pb	A	2 —	$^3P_{012} \quad ^1\bar{P}_{12} \quad ^1\bar{S}_0$
		B	1 1	$^3P_{012} \quad ^1\bar{P}_1$
N+2	N, P Bi	A	3 —	$^4S_2 \quad ^2D_{23} \quad ^2\bar{P}_{12}$
		B	2 1	$^4P_{123} \quad ^2P_{12} \quad ^2\bar{D}_{23} \quad ^2\bar{S}_1$
N+3	O, S Po	A	4 —	$^3P_{210} \quad ^1\bar{D}_2 \quad ^1\bar{S}_0$
		B	3 1	$^5S_2 \quad ^3S_1 \quad ^3D_{123} \quad ^1D_2 \quad ^3\bar{P}_{012} \quad ^1\bar{P}_1$
N+4	F, Cl	A	5 —	$^2P_{21}$
		B	4 1	$^3\bar{P}_{221} \quad ^2\bar{P}_{21} \quad ^2D_{32} \quad ^2S_1$
N+5	Ne, Ar Nt	A	6 —	1S_0
		B	5 1	$^5P_{210} \quad ^1P_1$

* N=5, 13, 31, 49, and 81 for atoms in the 1st, 2nd 5th short periods respectively.

By an electronic transition resulting in a change of configuration from that given in row B to that in row A in Table I., resonance wave-lengths of the arc spectrum are emitted. The most fundamental resonance line or most easily excited wave-length should be that involving the underlined terms in each spectrum, and hereafter we shall refer to this line only as the resonance line. In nearly all

the arc spectra that are being considered here the resonance line has been identified and shown to be classified by means of the terms underlined in Table I.

While considering the relations between the resonance lines in the various arc spectra the writers observed a well-defined periodicity in the progression of frequency with atomic number in each period, and also a similarity in the periodicities of each of the periods.

We consider that these regularities are well worth pointing out, not only from the standpoint of a practical application of the results to spectral analysis, but also on account of a suggestion their discovery raises of a new problem that should be of considerable interest to theoretical physicists.

II. Results.

The frequency, wherever it has been identified, of the resonance line in each of the arc spectra of the elements that are being considered is given in Table II. In this table the transition, which is the same in all atoms of the same period, of the most loosely-bound electron that results in the emission of the resonance wave-length is indicated, as well as the term classification, which is similar for arc spectra of all atoms of the same chemical group. The values in the arc spectra of the halogen atoms are not those of the resonance line ${}^2P_2 - {}^4P_3$, predicted in Table I. as this has not yet been identified. While the frequency for FI has been classified definitely as ${}^2P_2 - {}^2\bar{P}_2$, those for Cl I, Br I, and I I are uncertain and may be either ${}^2P_2 - {}^2\bar{P}_2$ or ${}^2P_2 - {}^4\bar{P}_2$. The term 4P_3 , however, should be a little deeper than either ${}^2\bar{P}_2$ or ${}^4\bar{P}_2$, so that the frequency values contained in Table II. are probably a little greater than that of the resonance line. Since the arc spectra of Po, Nt, and of the element of atomic number 85 have not yet been analysed, no values are available for the lines required in any of them.

An authority for the value and term classification of each frequency in Table II. is cited in the list of references at the conclusion of the paper.

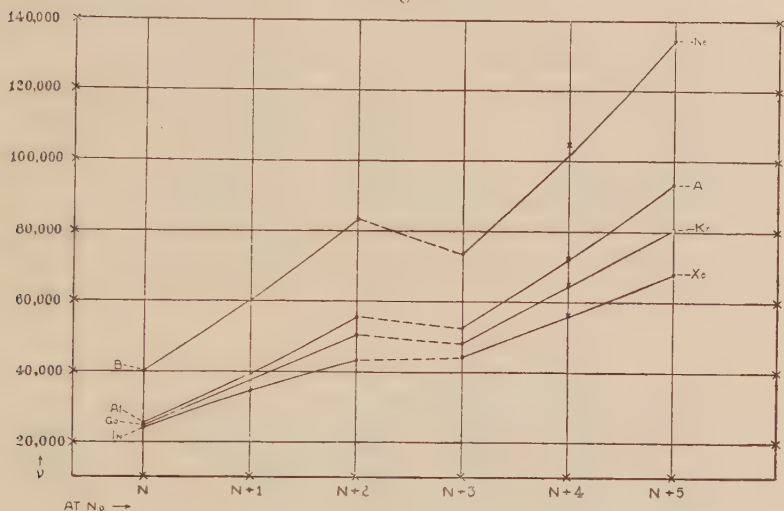
The arrangement of values in Table II. shows the progression of frequency with atomic number in each period, and also shows that it is qualitatively similar in at least each of the first four periods. The results are perhaps more clearly illustrated in fig. 1, where the frequencies, given in Table I., are

TABLE II.

Electron Transition		$31 \rightarrow 22$		$41 \rightarrow 32$		$51 \rightarrow 42$		$61 \rightarrow 52$		$71 \rightarrow 62$	
Term Class ⁿ .		El ^t .	ν .	El ^t .	ν .	El ^t .	ν .	El ^t .	ν .	El ^t .	ν .
$2P_1 - 3S_1$	ν_1 $\Delta\nu_{21}$	B	40,040 20,275	Al	25,348 14,258	Gd	24,788 12,914	In	24,373 10,541	Tl	26,478 8,808
$3P_0 - 3P_1$	ν_2 $\Delta\nu_{32}$	C	60,315 22,971	Si	39,606 16,338	Ge	37,702 12,992	Sn	34,914 8,335	Pb	35,287 -2,699
$4S_2 - 4P_1$	ν_3 $\Delta\nu_{43}$	N	83,286 -9,526	P	55,944 -3,325	As	50,694 -2,507	Sb	43,249 1,004	Bi	32,588
$3P_2 - 5S_2$	ν_4 $\Delta\nu_{54}$	O	73,760 30,976	S	52,619 19,865	Se	48,187 16,715	Te	44,253 11,836	Po	—
$2P_2 - P_2$ or $4P_2$	ν_5 $\Delta\nu_{65}$	F	104,736 29,763	Cl	72,484 21,254	Br	64,902 16,017	I	56,089 11,961	—	—
$1S_0 - 3P_1$	ν_6	Ne	134,499	Ar	93,738	Kr	80,919	Xe	68,050	Nt	—

plotted against atomic number and a curve obtained for each period. As we have pointed out, the values for the halogen atoms are a little higher than those needed. Therefore, the curves have not been drawn through the plotted points designated by \times but a little below each one.

Fig. 1.



III. Discussion of Results.

It is immediately evident either from a consideration of the progression of frequencies in Table II. or the curves in fig. 1, that for any of the first four periods

$$\Delta\nu_{21} \div \Delta\nu_{32} < \Delta\nu_{54} \div \Delta\nu_{65},$$

and that there is a discontinuity in the regular progression due to the negative or small positive value of $\Delta\nu_{43}$.

Now the resonance frequencies of the arc spectra of elements of the short periods of atomic numbers N to $N+5$ should be a measure of the relative strength of binding of an outermost electron in an n_2 orbit when one ... six of these orbits are occupied with the atom neutral and in the normal state.

If all equivalent n_2 orbits in an atom were similar then the curves in fig. 1 would be expected to be continuous ones. But in each curve there is a well-defined discontinuity. This discontinuity probably has a close relationship to another well-known feature in the arc spectra of these

elements, namely, that for deep-lying multiple terms of the arc spectra of the elements of atomic numbers N to $N+2$ the components are in the normal order, while for elements with atomic numbers $N+3$ to $N+5$ they are inverted.

It seems probable that both the features mentioned above are due to the fact that n_2 orbits are of two types, that have been designated n_{21} and n_{22} orbits characterized by the inner quantum numbers $j = \frac{1}{2}$ and $j = \frac{3}{2}$ respectively; and that in a neutral atom of atomic number N , $N+1$, or $N+2$ the n_{21} orbits are more stable, while in one of atomic number $N+3$, $N+4$, or $N+5$ the n_{22} orbits are more stable. Whether or not the two discontinuities mentioned, that occur between the third and fourth elements of each short period of six, indicate that the maximum number of electrons that can occupy orbits of the n_{21} and n_{22} types is three and three respectively, as against the numbers two and four proposed by Stoner, we are not at present able to say.

IV. *Conclusion.*

In the preceding sections the relative strength of binding of an outermost electron in an n_2 orbit in neutral atoms that have one ... six equivalent n_2 orbits occupied, has been determined by a consideration of the resonance lines of the arc spectra of a number of elements.

The strength of binding of an outermost n_1 electron when there are one or two of these in an atom has, of course, long been recognized, the latter being more tightly bound than the former.

It would be interesting to determine the binding of equivalent n_2 electrons in ionized atoms and of equivalent n_3 or n_4 electrons in either neutral or ionized atoms, but there are not sufficient data to make this possible at the present time. It is to be hoped that this deficiency will be made up shortly and that further observations of a similar nature to those outlined in the preceding sections will help to throw some further light on the significance of the present results.

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The Physical Laboratory,
University of Toronto,
June 30th, 1927.

XXXVII. *Notices respecting New Books.*

Stars and Atoms. By A. S. EDDINGTON, M.A., D.Sc., LL.D.,
F.R.S. Pp. 127 with 11 figures. (Oxford: Clarendon Press,
1927. Price 7s. 6d. net.)

THIS volume contains the substance of three lectures delivered in King's College, London, in 1926, and of an Evening Discourse at the meeting of the British Association in the same year. It deals largely with the author's researches on the internal constitution of the stars, and will serve as a fitting introduction to his larger book, 'The Internal Condition of the Stars,' in which the subject is treated mathematically.

The volume is divided into three lectures, entitled respectively The Interior of a Star; Some Recent Investigations; The Age of the Stars. The basic idea throughout is the interdependence of atomic physics and stellar physics. The progress in our understanding of the conditions which prevail inside a star is dependent upon advances in our knowledge of atoms and radiation. Reciprocally, the clearer understanding which has been thus gained of the conditions in the stars, where matter is under extreme conditions which cannot be duplicated in the laboratory, has contributed in no small measure to the progress of atomic physics.

Professor Eddington's unique power of clear exposition is well known. In this volume he succeeds in conveying to the non-mathematical reader a clear idea as to how mathematical treatment can lead to conclusions about the deep interior of a star, where neither the eye nor the telescope can penetrate. His detective stories, "The Missing Word and the False Clue" and "The

Nonsensical Message," read like real romances, and serve to bring home to the reader some of the difficulties encountered by the way.

The number of really well-written popular books of science is very small. We have no hesitation in classing this volume amongst the best of them. Prof. Eddington writes with an excellent style, and the compelling force of his reasoning, aided by simple illustrations and analogies, renders the volume easy and fascinating to read. Once it is taken up, it will be found difficult to lay it aside before the end is reached.

It is not every scientific worker who has the gift of writing an account in popular language of his own investigations. Professor Eddington has that gift, and we are glad that he has found time to make some of his results available in a book which can be read by a wider circle of readers than his mathematical treatise on the same subject.

Applied X-Rays. By GEORGE L. CLARK, Ph.D. (McGraw-Hill Publishing Co. 255 pp., 99 figs. Price 20s. net.)

MR. CLARK, who writes from the Massachusetts Institute of Technology at Boston, has compressed an extremely large amount of information into his book, and has succeeded in presenting it in logical and attractive fashion. The first two sections of the volume deal, here and there perhaps a little cursorily, with the means of generating X-rays, the measurement of intensity, the absorption and scattering of X-rays, the fundamentals of X-ray spectroscopy, and the protection of the X-ray worker. The chemical and biological effects of X-rays and their radiographic applications, both industrial and medical, are dismissed in two short chapters.

The third and largest section, covering some 150 pages, is devoted to the applications of X-ray crystal analysis. The literature of this subject is now very large, and is growing rapidly, but Mr. Clark makes an enthusiastic and praiseworthy attempt to summarize the situation to date. It is premature to generalize too freely, the technique is still being developed, and the potentialities and limitations of the method are gradually being revealed; but the list of achievements is already sufficiently impressive to warrant high expectations for the future of X-ray spectroscopy in many walks of industry. At the moment, metallurgy would perhaps appear to offer the greatest scope for the X-ray spectroscopist, the physical and chemical properties of many metals and alloys providing tempting and doubtless tantalizing problems.

While this country has every reason to be well satisfied with its contributions to the fundamentals of X-ray crystal analysis, it would not appear from Mr. Clark's book that a like attention has been paid to the industrial applications. Matters are evidently very different both in the States and Germany; but there are grounds for hope that in the near future the situation will rectify itself on this side of the water.

The Calculus of Variations. By A. R. FORSYTH. (Cambridge University Press. Price 50s. net.)

WE have at last before us a work which every physicist whose work has dealt in any way with the Principle of Least Action, and certainly every mathematician, like the present writer, who has been called upon to teach this subject, has longed for. The Calculus of Variations has always consisted, in any possible presentation, of a series of fragmentary investigations aimed at the solution of specific historical problems—for example, the brachistochrone, the solid of least resistance, and so forth. The limitations of validity of these solutions have never been clear. The usual course has been to make a final appeal to Todhunter's History of the Calculus of Variations, which deals with all the more classical problems which invoke this mode of procedure, but with all the limitations of validity pertaining to that time. We consider that, by welding the whole subject together in this volume, as a connected account, Prof. Forsyth has probably done greater service to the mathematician and physicist than he even did in his treatises on the theory of Differential Equations and on Differential Geometry.

Much of the work in this book has hitherto been entirely inaccessible. Some of the most fundamental, really defining the limitations—"grave," as the author repeatedly states,—on some of the solutions commonly accepted, including even the Principle of Least Action—have existed only in manuscript form, as notes of lectures by Weierstrass, who made vast improvements on all the work preceding him. The author has had access to many such sources, and has now really created a new branch of mathematics of a self-contained type. Teachers of mathematics in the Universities will now, for the first time, be able to point the Calculus of Variations out to a pupil as a subject in which further progress is possible in many indicated directions. The book should be a valuable stimulus to many who wish to take up post-graduate research work.

The treatment is exhaustive. We miss nothing with which we were previously familiar, but we always find ourselves able to learn something from the manner in which it is presented. The general format of the book is in the best traditions of the Cambridge University Press.

Differential Geometry of Three Dimensions. By C. E. WEATHERBURN. (Cambridge University Press. Price 12s.)

THE present volume provides an introductory treatise on Differential Geometry, and shows how vector methods may be employed with great advantage. The author is evidently indebted to Forsyth and Eisenhart as well as to the Continental Geometers. But there is a real need for a volume of this sort. It will be found very suitable for first year University students, and a large number of examples are introduced into the work.

The early chapters deal with curvature and torsion, envelopes, developable surfaces, and curvilinear co-ordinates.

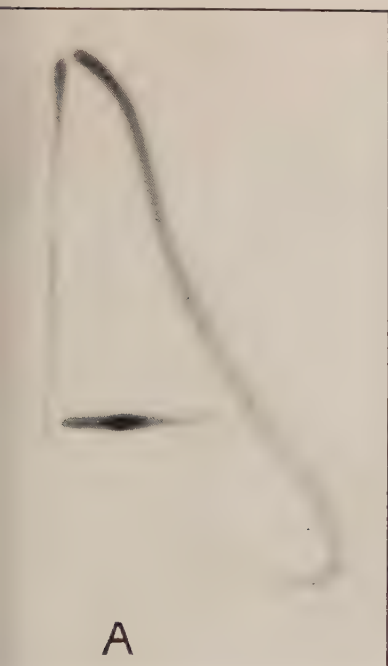
Geodesics on Quadric surfaces are next dealt with; and finally, after a discussion of conformal and spherical representations and other cognate topics, the author concludes with a chapter entitled "Further Recent Advances." In this concluding chapter the author gave an account of several important additions to our knowledge of the properties of families of curves and surfaces which he has most recently made. When the book was nearly completed, and the author had decided to avoid introducing the so-called "Beltrami's" differential parameters, in spite of their importance in many directions, he discovered that they were, in fact, individual members of a large family whose significance had hitherto been missed. Accordingly, several of the later sections were re-written, and contain work which cannot be found elsewhere. The value of the book is considerably enhanced; and though the author does not promise this, it may be hoped that further developments in this promising direction may take place and ultimately lead to a supplementary volume. The work can be recommended with confidence to a student with a liking for vectorial notation and treatment who wishes to obtain a thorough knowledge of Modern Differential Geometry.

Three Lectures on Atomic Physics. By A. SOMMERFELD. (Translated by H. L. Brose.) (Methuen & Co. Price 2s. 6d.)

THE present book comprises lectures given in the University of London dealing with the recent developments of the Quantum Theory. In the first Quantum numbers n , k , l , m , etc. are introduced, and a new interpretation of the Hydrogen Spectrum is given. The next lecture deals with the general construction of terms of any Multiplicity, with the definition of primed and unprimed terms and their selection rules, and with Pauli's principles of uniqueness. Finally, the periodic system of the elements is dealt with and also the tetrahedral crystal structure of certain elements of the fourth group.

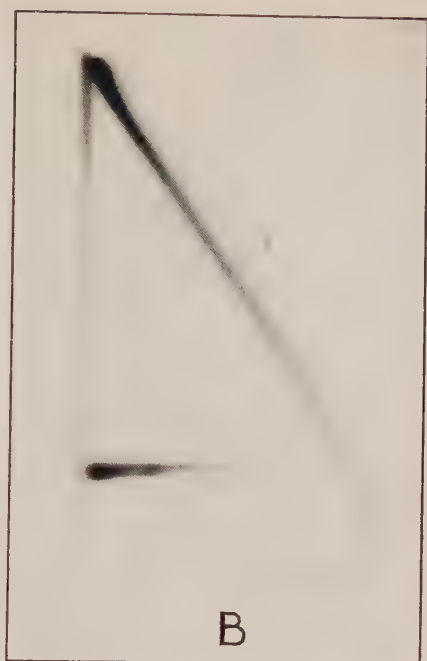
It will be a great advantage to students of Modern Physics to have this little book in its translated form. The lectures were originally given in London, though Prof. Sommerfeld also gave similar lectures elsewhere. As a compendium of current views on the exact position of the Quantum Theory in the mind of one of its most vigorous exponents, they have no parallel. Mr. Brose, the translator, is to be congratulated on the reproduction, in his translation, of the very attractive style which, in a verbal form, delighted those who had the good fortune to hear Prof. Sommerfeld during his visit to England.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]



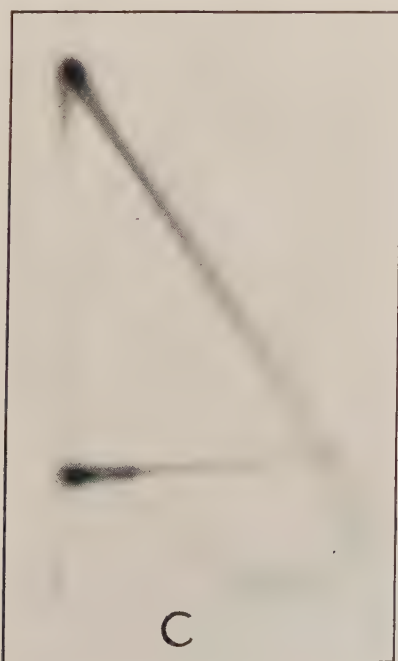
FORK SOUNDING.

Frequency of flashing increased.

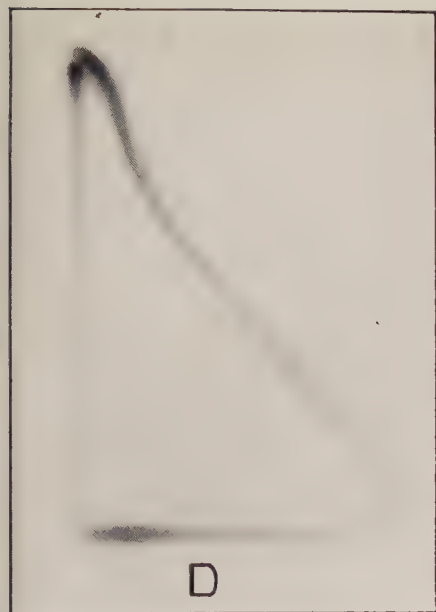


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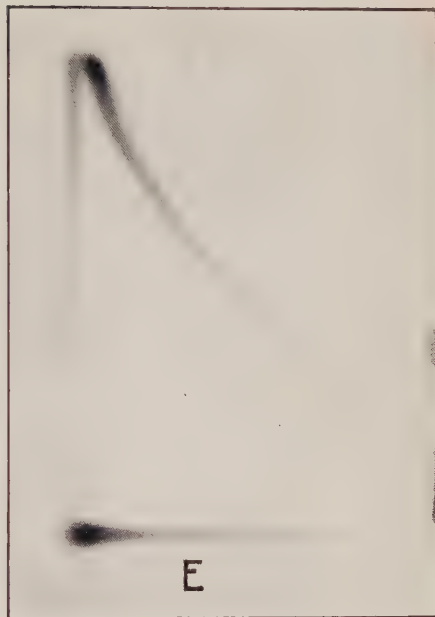
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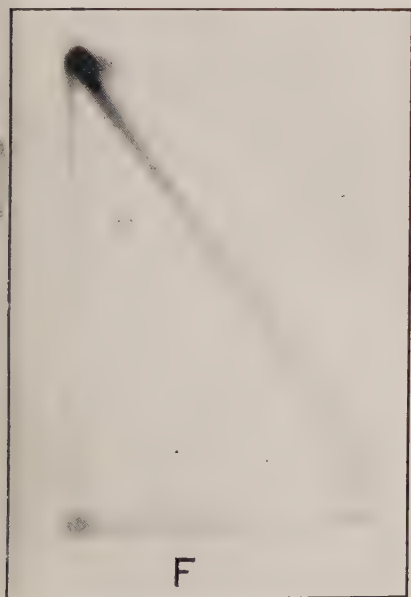
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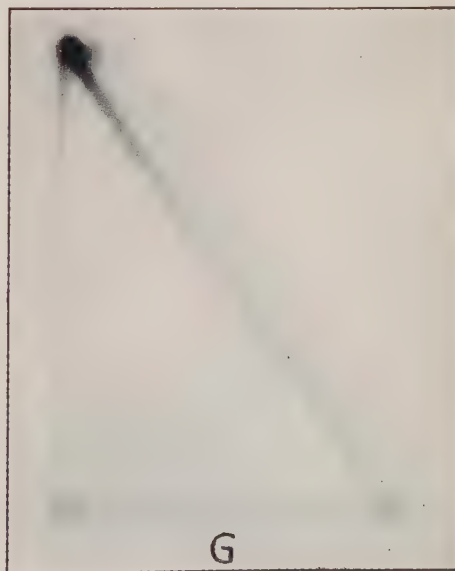
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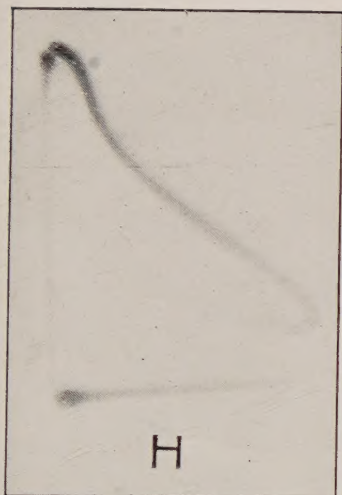
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G

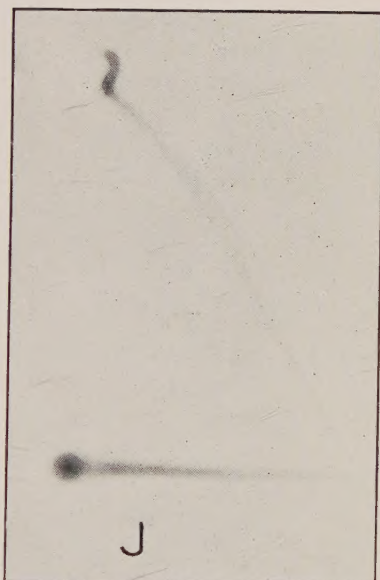
INDUCTANCE REMOVED FROM CIRCUIT.



I-type lamp.

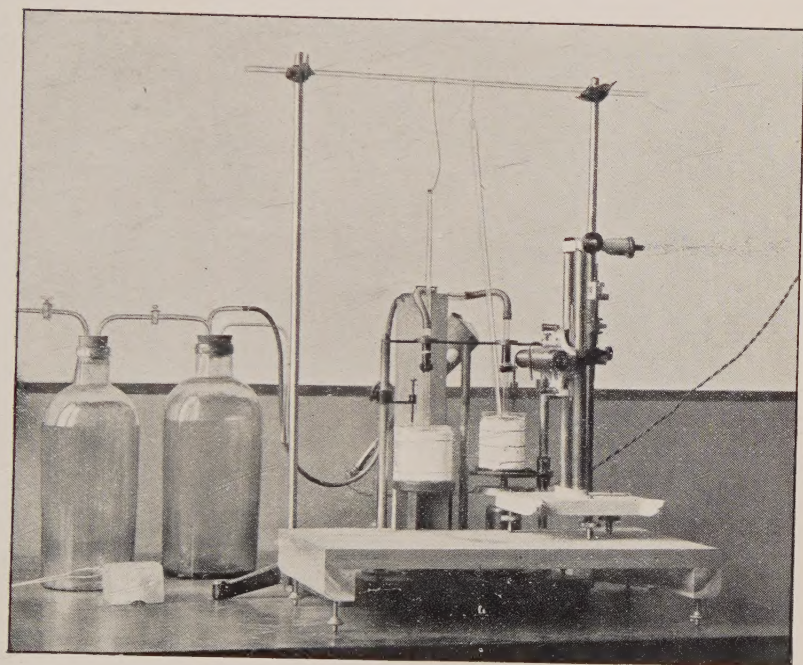
FORK SOUNDING.

Frequency of flashing increased.



FORK SOUNDING.

Frequency of flashing one-half the frequency of the Fork.



THE SURFACE-TENSION BALANCE.

